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COMMUNICATION

Improving the energy yield of plasma-based NO_x synthesis with *in situ* adsorptionKevin Hendrik Reindert Rouwenhorst^{a,b,c} Siebe Tabak^a and Leon Lefferts^{a*}Received 00th January 20xx,
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Plasma-based NO_x synthesis from air is a promising option to electrify nitrogen fixation. However, the energy efficiency of direct plasma-based NO_x synthesis in a plasma reactor is severely limited by NO_x decomposition in the plasma phase. *In situ* NO_x adsorption on MgO improves the NO_x energy yield in a dielectric barrier discharge (DBD) plasma reactor by a factor of 15.

Plasma-based nitrogen fixation via NO_x synthesis from air was commercialized in the early 20th century. Kristian Birkeland and Samuel Eyde commercialized the first industrial nitrogen fixation process, the Birkeland-Eyde process, based on an electric arc plasma reactor^[1,2]. This process was operational in Norway and Canada^[3,4]. However, the process was eventually outcompeted by the Haber-Bosch process, producing ammonia (NH₃) from nitrogen (N₂) and hydrogen (H₂) derived from steam reforming of hydrocarbons or from water electrolysis.

Plasma-based nitrogen fixation has re-emerged in scientific literature as an option to electrify N₂ fixation^[5–9]. Plasma-based processes have the advantage that the load can be varied quickly, in contrast to thermal processes, so that rapid changes in supply of renewable electricity can be handled^[10]. Also, absence of the need for intensive energy integration makes local production at relatively small scale feasible. In particular, plasma-N₂ fixation in the form of NO_x shows promise^[5,6].

So far, plasma-based NO_x synthesis in warm plasma reactors such as gliding arc (GA) and microwave (MW) plasma reactors,

shows the best performance^[5,6], with NO_x formation at an energy cost down to 0.42 MJ/mol-NO_x^[11], which is competitive with the renewable Haber-Bosch process (using electrolysis to produce H₂) combined with the Ostwald process (NH₃ oxidation) in terms of energy cost (0.6 MJ/mol-HNO₃)^[6]. However, such low energy consumptions for plasma reactors are only achieved when operating at low NO_x concentrations of typically a few hundred ppm^[11], which is not practical for NO_x absorption in water in an industrial process^[12]. Concentrations in the order of 5 mol.% NO_x are required for efficient processing. For those conditions, the energy consumption for NO_x formation in plasma reactors is at least in the order of 2 MJ/mol-NO_x^[6]. Furthermore, the high temperatures in warm plasmas in the order of 10³ K cause thermal NO_x decomposition^[13] and rapid quenching is required to minimize thermal NO_x decomposition.

This work introduces a novel concept for energy-efficient NO_x formation in a dielectric barrier discharge (DBD) reactor via *in situ* NO_x removal using a solid MgO sorbent. A DBD reactor is a non-thermal plasma reactor operating near room temperature^[14]. Only a few studies have been done using DBD reactors for NO_x synthesis^[13,15–18], reporting relatively high energy consumption compared to warm plasma reactors. Nevertheless, a DBD reactor has been used in this work for two reasons. Firstly, thermal NO_x decomposition is negligible at mild temperature, and secondly, *in situ* NO_x removal via adsorption on a solid sorbent is easily achievable. Product molecules adsorbed on microporous materials are protected against plasma induced decomposition in a DBD reactor, as we have demonstrated earlier for the case of ammonia synthesis in a DBD reactor^[19]. Plasma cannot develop in sub-micron pores while plasma activated species are too short-lived to diffuse into these pores; therefore adsorbed molecules are protected against plasma-decomposition^[8]. Suppressing NO_x decomposition is expected to improve both energy efficiency and the single pass conversion in a DBD reactor. As earth-alkali

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Electronic Supplementary Information (ESI) available: Experimental procedures, including materials and preparation, material characterization, plasma characterization, NO_x synthesis and adsorption experiments. Results & discussion, including material characterization, plasma characterization, thermal NO_x TPD study with MgO, and energy cost for MgO regeneration. See DOI: 10.1039/x0xx00000x



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metal oxides are known to sorb NO_x [20], we have selected MgO to demonstrate this concept. We will show that both energy efficiency as well as NO_x concentrations in the product stream are drastically improved.

High surface area MgO (294 m^2/g) with a particle size between 250 and 300 μm was prepared and characterized as described in supporting information section S1. The experiments were performed using a packed bed DBD reactor with MgO particles, and the NO_x concentration was determined with a Mass Spectrometer (MS), as described in detail in supporting information section S2.1.

Fig. 1 shows the NO_x concentration in the outlet as a function of time on igniting the plasma, operating with an $\text{O}_2:\text{N}_2$ ratio of 1:1, flow rate of 20 mL min^{-1} , plasma power of 6.4 W, implying a SEI (specific energy input) of 19.2 kJ L^{-1} . The corresponding Lissajous plot is shown in Fig. S3 (see ESI). It is observed that the NO_x outlet concentration is about 0.1 mol.% during the first 4 min and increases to about 0.5 mol.% afterwards. The change in NO_x outlet concentration with time in Fig. 1 is attributed to adsorption of NO_x on the MgO sorbent, followed by breakthrough of the NO_x in the outlet.

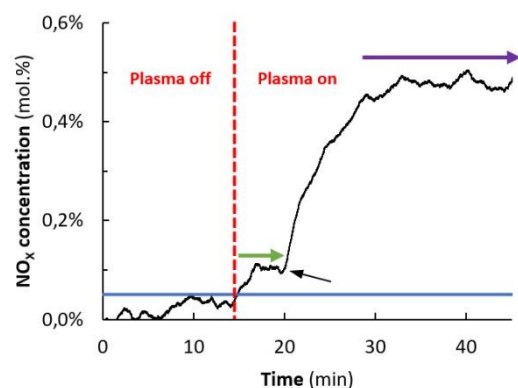


Fig. 1 Outlet NO_x concentration as a function of the plasma duration. Oven temperature set point, 25°C; total flow rate, 20 mL min^{-1} ; $\text{O}_2:\text{N}_2=1:1$; plasma power, 6.4 W (SEI = 19.2 kJ L^{-1}); MgO loading, 300 mg (250-300 μm). The blue line represents the MS Sensitivity Limit. The green arrow line indicates *in situ* NO_x removal with MgO. The black arrow indicates breakthrough of NO_x due to sorbent saturation. The purple arrow indicates steady-state operation.

The result shown in Fig. 2 confirms that NO_x is indeed adsorbed *in situ*. After exposure to the plasma, the reactor was heated (25°C min^{-1}) in N_2 (10 mL min^{-1}), inducing desorption of NO_x in absence of plasma. The concentration of NO_2 is much higher than NO , but we cannot rule out NO formation, as explained in SI 3.3. The NO_x concentration during desorption is up to 4%, one order of magnitude higher than the NO_x concentration during steady-state plasma operation. The amount adsorbed NO_x is 0.05 mol per mol MgO.

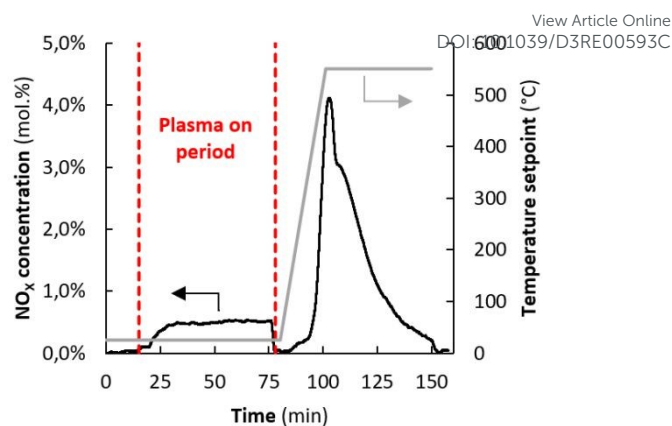


Fig. 2 Typical result of plasma-based NO_x synthesis with in-situ adsorption. Reactor temperature (left axis) and outlet NO_x MS signal (right axis) as a function of time. Oven temperature set point during plasma, 25°C; total flow rate, 20 mL min^{-1} ; $\text{O}_2:\text{N}_2=1:1$; plasma power, 6.4 W (SEI=19.2 kJ L^{-1}); MgO loading, 300 mg (250-300 μm); plasma duration, 63 min; heating rate after plasma-based NO_x synthesis, 25°C min^{-1} ; pure N_2 , 10 mL min^{-1} . Samples are thermally pre-treated at 550°C in N_2 .

Fig. 3 compares the TPD (Temperature Programmed Desorption) result after NO_x synthesis by plasma illumination during different times with TPD after adsorption of NO_2 at room temperature. The amount of NO_x formed during the plasma experiment obviously varies with plasma time. Fig. 4 shows that the amount of NO_x detected with TPD is already saturated after typically 5 minutes of plasma exposure. The amount is slightly lower than after thermal NO_2 adsorption in absence of plasma (0.055 mol- NO_2 mol-MgO $^{-1}$), in the same order of magnitude as reported by Duong et al. [21] for MgO with a slightly lower surface area of 126 m^2/g . The lower amount observed during NO_x synthesis with plasma is likely attributed to mild heating induced by the plasma, causing weakly adsorbed NO_2 to desorb. A similar effect was previously reported for *in situ* NH_3 removal by a zeolite for plasma-based NH_3 synthesis [19]. The effective NH_3 capacity on zeolite 4A decreased by 60% due to heating effects [19].

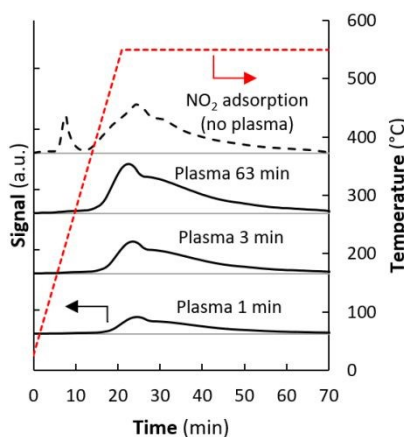


Fig. 3 TPD curve results after plasma-based NO_x synthesis ($\text{O}_2:\text{N}_2=1:1$, plasma duration varied: 1 min, 3 min & 63 min), flow rate 20 mL min^{-1} compared to TPD curve after adsorption of NO_2 at room temperature (2 vol.% NO_2 in 10 vol.% O_2 and 88 vol.% N_2 balance gas during adsorption). TPD in pure N_2 , 10 mL min^{-1} and heating rate 25°C min^{-1} .



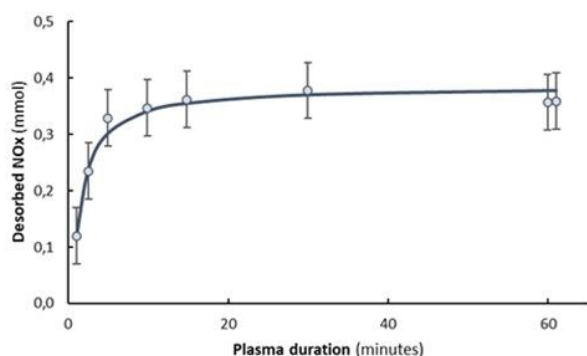


Fig. 4 The effect of plasma duration for plasma-based NO_x synthesis with *in situ* adsorption on the amount of adsorbed NO_x on 300 mg MgO.

The significance of the *in situ* adsorption of NO_x from the plasma zone is evident from the reduction in energy consumption versus steady-state operation. Steady-state NO_x synthesis in this work results in an energy consumption of 93 MJ mol-NO_x⁻¹, in line with literature values reported in the range 16–540 MJ mol-NO_x⁻¹ for DBD reactors [13,15–18]. In case of *in situ* product removal during 5 minutes, the energy consumption for the plasma reactor and NO_x product desorption decreases to 6.0 MJ mol-NO_x⁻¹ as calculated in supporting information section S3.2 including the energy cost of the desorption step. Effectively, the energy consumption efficiency is improved by a factor 15. As shown in Fig. 5, *in situ* adsorption of NO_x in a DBD reactor results in the best performance for a non-thermal plasma-reactor, by both decreasing the energy consumption as well as increasing the NO_x concentration in the product stream. Importantly, the NO_x concentration raised well above 1%, which is considered as the minimum concentration required for nitric acid production by adsorption in water in a commercially viable process [22].

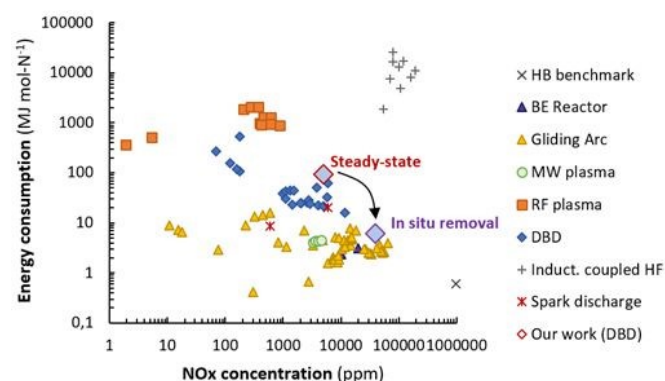


Fig. 5 Comparison of energy consumption for NO_x production in various plasma reactors. Original figure reproduced from ref. [6], and data from this work added. Steady-state: red lined diamond. In situ removal: purple lined diamond.

Concluding, this work demonstrates that low temperature DBD plasma reactors can produce NO_x with similar low energy consumptions obtained with warm plasma reactors like gliding arc reactors and microwave reactors (Fig. 5), by integrating plasma conversion and product separation. Also, the NO_x concentration in the product stream is significantly increased. This study demonstrates the concept, but optimization of the

(earth-) alkali material as well of the morphology of the adsorbent is likely to result in further improvement.

Furthermore, addition of a catalyst [23], optimization of the dielectric properties of the adsorbent [18], and optimization of the plasma properties could be considered [24,25].

In situ product removal is relevant for the wider scientific community working on plasma-(catalytic) conversion. We demonstrate that a significant improvement for NO_x synthesis and it is likely that the concept would also applicable for plasma-based CO₂ dissociation and CH₄ conversion [26].

Conflicts of interest

There are no conflicts to declare.

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