Applied Catalysis B: Environmental 100 (2010) 427–432

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Review

Solid state electrochemical DeNO$_x$—An overview

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ARTICLE INFO

Article history:
Received 9 July 2010
Received in revised form 30 August 2010
Accepted 2 September 2010
Available online 15 September 2010

Keywords:
N_2O
NO
NO_2
O_2
Electrochemical DeNO$_x$

ABSTRACT

The literature on direct electrochemical reduction of NO$_x$ in a solid state cell has been reviewed. It is shown that the reduction of nitric oxide either occurs on the electrode or on the electrolyte if F-centers are formed. It is also shown that some oxide based electrodes has a high apparent selectivity towards the reduction of nitric oxide in a net oxidizing atmosphere. The activity and apparent selectivity of oxide based electrodes is strongly dependent on the composition of the oxide. The selectivity of noble metal based electrodes is generally very low. However, coating of noble metal based electrodes can give current efficiencies of up to 20% even in the presence of large amounts of oxygen.

Contents

1. Introduction

The exhaust gas emitted from the combustion process of fossil fuels contains significant amounts of NO$_x$ [1]. The emission of NO$_x$ is highly unwanted, as NO$_x$ lead to the formation of smog and acid rain [2,3]. Several processes are known that can reduce the NO$_x$ from diesel exhausts. The best known commercial solution is the selective catalytic reduction (SCR) of NO$_x$ using urea as a reducing agent [4]. The main problems with this method is that the reducing agent has to be stored on-board the vehicle, and that possible slip of the reducing agent is a serious threat. The formation of nitrous oxide (a powerful greenhouse gas) is another problem, that hasn't been solved [5]. Electrochemical reduction of NO$_x$ in an all solid state electrochemical reactor is a potential attractive technique [6]. In electrochemical reduction of NO$_x$ current is used instead of a reducing agent. The concept is shown in Fig. 1. In the figure it is seen that nitric oxide is reduced at the cathode to nitrogen and oxide anions. The oxide anions are transported through the electrolyte to the anode where oxygen is formed. Some reviews on solid state electrochemical DeNO$_x$ have already been published most of them several years ago [6–10]. This is an up to date and more in depth review.

2. General considerations

The constituents and the temperature of the exhaust of different types of engines are shown in Table 1. It is seen that the exhaust of a typical diesel engine contains 200–1000 ppm of NO$_x$, besides other pollutants. In this context the high amount of oxygen present in the exhaust gas should be noted.

Solid state electrochemical DeNO$_x$ is build on the SOFC technology. The operation temperature of the SOFC is typically around 750 °C. The temperature of the exhaust gas of a diesel engine is much lower, 300 °C or even lower. Questions on the activity arise from this. The activity is therefore one problem that has to be tackled to make solid state electrochemical DeNO$_x$ useful for practical applications.

The high amount of oxygen is another issue to be addressed. Oxygen can be reduced along with nitric oxide at the cathode. If oxygen is reduced before nitric oxide this will lead to a very low

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doi:10.1016/j.apcatb.2010.09.002

Table 1
The constituents in different exhaust gasses.

	CO (%)	HC (ppm)	NO_x (ppm)	Particulate (g kWh^{-1})	O_2 (%)	Temp. (°C)
Otto	0.3–1	1000–5000	50–2500	–	0.1–0.5	150–1000
Otto lean-burn	0.05–0.5	1000–5000	100–1000	–	0.5–5	100–900
Diesel	0.01–0.2	100–2000	200–1000	0.15–0.5	3–15	80–700

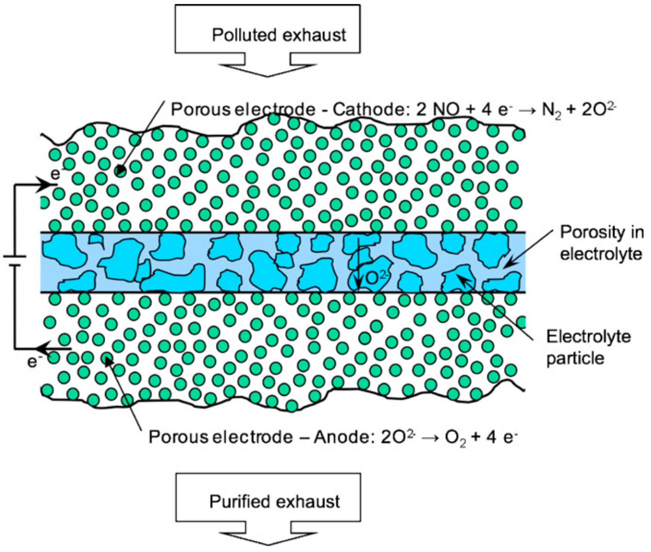

Fig. 1. A sketch of an electrochemical reactor for removal of nitric oxide. The reactor is seen to consist of an electrolyte and a pair of electrodes. The reduction of nitric oxide occurs at the cathode.

current efficiency. The selectivity is therefore another issue that has to be solved before solid state electrochemical $DeNO_x$ can be made a success. Almost all the literature concerning solid state electrochemical $DeNO_x$ has focused on the selectivity.

In Fig. 2 theoretical calculations on the extent of reaction as a function of potential at 400 °C is shown. It is seen that the reduction of nitric oxide to nitrogen is initiated at very high potentials, approximately 0.5 V vs. air, compared to the potential where the reduction of oxygen is initiated. This is also illustrated in Fig. 3. It is seen that the anti-bonding orbitales of nitric oxide is placed at a lower energy level than the anti-bonding orbitales of oxygen that

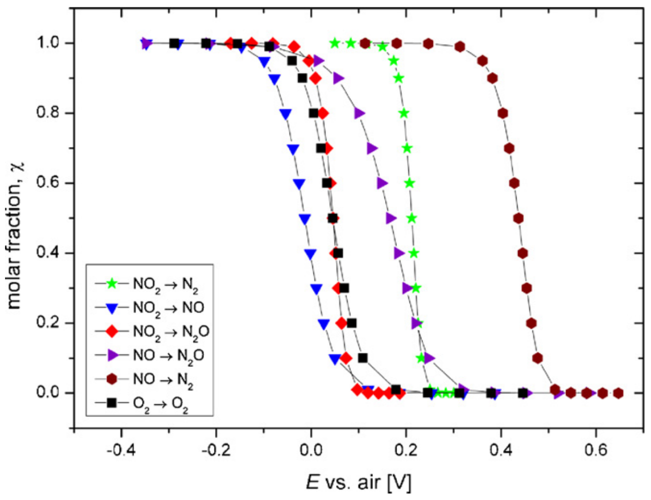

Fig. 2. Extent of reaction as a function of potential for different gaseous reactions. The black squares are representing the oxygen exchange reaction, which is pumping of oxygen of from one side of the cell to the other side of the cell. The higher the potential is the lower is the relative stability of the given molecule.

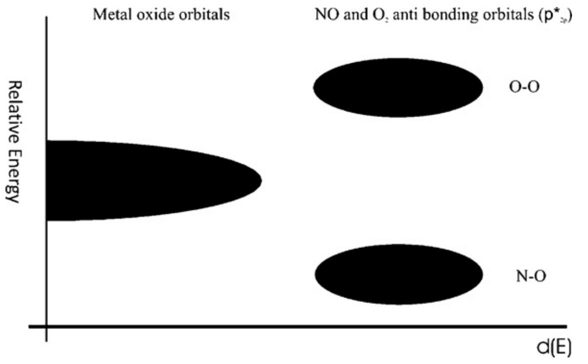

Fig. 3. Schematic picture of the energy level of the valence electrons of a metal oxide and the anti-bonding orbitales of nitric oxide and oxygen. The $d(E)$ on the x-axis denotes the density of states.

is nitric oxide is less stable than oxygen. It is also seen from Fig. 2 that the reduction of nitric oxide to nitrous oxide is initiated at a lower potential than the reduction of nitric oxide to nitrogen. Based on thermodynamic considerations alone it is therefore possible to reduce nitric oxide selectively to nitrogen by a careful control of the applied potential. However, oxidation of nitric oxide to nitrogen dioxide must also be taken into account. As it can be seen from Fig. 2 nitric oxide is oxidized to nitrogen dioxide at potentials above approximately 0 V vs. air. This is the same as saying that nitric oxide is thermodynamic unstable at 400 °C, as nitric oxide can be reduced and oxidized in the same potential window.

3. Literature survey

Early work. The idea of reducing NO_x electrochemical in an all solid state cell was first suggested by Pancharatnam et al. [11] in 1975. Using a Scandia Stabilized Zirconia (SSZ) electrolyte and either porous platinum or porous gold electrodes they showed that nitric oxide could be reduced at the cathode to N_2 and oxide anions in the temperature range of 600–800 °C. By applying very high overpotentials (−2.2. V vs. air) it was furthermore shown that the rate of the reduction of nitric oxide exceeded the Faradaic value by a thousand fold. The results indicated that the reduction of nitric oxide occurred on the zirconia surface and not on the electrodes. When high cathodic potentials are applied to a zirconia based cell, the zirconia is reduced (blackening). The blackening of zirconia is due to the formation of F-centers. The mechanism below was suggested by the authors

$$V_0^{\bullet\bullet}(s) \leftrightarrow V_0^x(s) + 2h_{\mathrm{electrode}}^{\bullet} \quad (1)$$

$$NO + V_0^{\bullet\bullet}(s) \rightarrow N\text{–}O_0^x(s) \quad (2)$$

$$NO + N\text{–}O_0^x(s) \rightarrow N_2O + O_0^x(s) \quad (3)$$

$$N_2O + V_0^x(s) \rightarrow N_2 + O_0^x(s) \quad (4)$$

$$O_0^x(s) + V_0^{\bullet\bullet}(b) \leftrightarrow V_0^{\bullet\bullet}(s) + O_0^x(b), \quad (5)$$

where V_0^x is a F-center, (s) denotes the surface of electrolyte and (b) the bulk of the electrolyte. In a later work by Gür and Huggins [12] this mechanism was confirmed using platinum and gold point electrodes.