Influence of nitrogen oxides on the electrocatalytic oxidation of sulphur dioxide

P. ILIEV, I. NIKOLOV, T. VITANOV, E. BUDEVSKI

Central Laboratory of Electrochemical Power Sources, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

The electrocatalytic oxidation of sulphur dioxide in the presence of nitrogen oxides (NOx) on active carbon catalysed with pyrolized cobalt phthalocyanine (CoPc) was investigated. It is shown that Nox block the catalyst surface without undergoing any electrochemical changes. This phenomenon leads to a partial decrease of the electrocatalytic process rate, i.e. the SO_2 removal efficiency.

1. Introduction

It is well known that atmospheric pollution by sulphur dioxide poses a great ecological problem. A main source of sulphur dioxide emissions is the waste gases from thermal power stations, as well as from metallurgical, oil refining and other chemical plants. Generally these gases contain nitrogen oxides (NOx), and this should be taken into account in the development of equipment for desulphurization of waste gases.

A method for desulphurization of waste gases (ELCOX process) has been developed in the Central Laboratory of Electrochemical Power Sources (CLEPS), Sofia, based on the electrocatalytic oxidation of sulphur dioxide by oxygen in air at 25–40° C [1]. The catalyst used is hydrophobic active carbon catalysed with pyrolized Co-phthalocyanine (CoPc) [2]. The reaction between sulphur dioxide and oxygen takes place on the three phase catalyst–electrolyte–gas boundary.

The aim of the present work was to establish the influence of the nitrogen oxides (NOx) on the rate of the electrocatalytic oxidation of sulphur dioxide, i.e. on the SO_2 removal efficiency of the ELCOX method. The studies were carried out using a mixture of nitrogen oxides (NO, NO_2, N_2O_4, N_2O_5), since all these are formed during fuel combustion processes.

There is abundant literature concerning the electrochemical behaviour of nitrogen oxide (NO) on platinum electrodes [3–5]. It was shown that at a potential of $+750\,mV$ (HE) this oxide is reduced to N_2O, while at $+350\,mV$ (HE) the reduction proceeds to NH_2OH [3]. According to Parsons et al. [5] adsorbed hydrogen atoms play an important role in this process.

2. Experimental details

The electrochemical measurements were performed in a three electrode cell (Fig. 1). The working electrode had the construction of a two-layered gas-diffusion electrode designed in CLEPS [6], the counter electrode was a Pb rod and the reference was Hg/Hg_2SO_4. The electrode studied was a "gas-diffusion tablet" consisting of two layers: the active layer containing "Norit SA" active carbon catalysed with 10 wt % CoPc and carbon black wetproofed with polytetrafluoroethylene (PTFE) as binding agent, while the gas-diffusion electrode was PTFE-treated carbon black. The electrode working surface area was $10\,cm^2$. The measurements were carried out under potentiostatic conditions using a Wenking LB 75 L potentiostat. The tests were performed in 0.5–4.5 M H_2SO_4. The choice of this concentration range was determined by the fact that in the ELCOX process the sulphur dioxide oxidation then proceeds at a rate suitable for its practical realization [1].

The measurements were carried out with gas mixtures produced by combining air or argon with sulphur dioxide and nitrogen oxides respectively. The SO_2 was fed from a pressurized vessel of liquefied SO_2, while NOx were obtained by a reaction of copper turnings with HNO_3. The SO_2 concentration was 2000–2200 p.p.m., while that of NOx was 900–1100 p.p.m. The values correspond to the average concentrations of those compounds in the waste gases emitted from thermal power stations using black oil.

Measurements were also performed in a test column for desulphurization of gas mixtures containing sulphur dioxide (Fig. 2). The column working volume was $1.5\,dm^3$. The 8 catalytic sheets mounted inside were produced by pressing the hydrophobized catalyst onto polyester felt cloth [1]. Their active surface area was $2400\,cm^2$ and the gas mixture flow rate was $250\,dm^3\,h^{-1}$ (8.3 s contact time). The gas flow and the electrolyte (sulphuric acid with continuous rise of concentration) were fed into the column in counter flow. The electrolyte flowed down along the polyester cloth wetting the hydrophobized catalyst on which the reaction between sulphur dioxide and oxygen takes place. The SO_2 removal efficiency is defined as the relationship of the SO_2 concentrations at the column outlet and inlet.

The SO_2 and NOx concentrations in the gas mixtures were measured using a computerized gas analyser MSI 2500 PT, Schwerte, Germany.
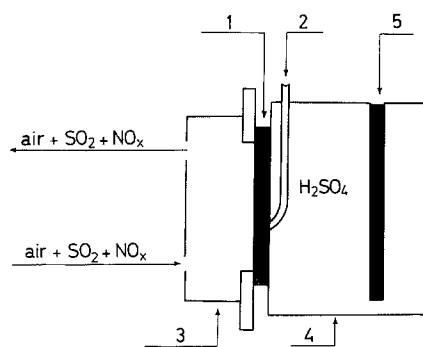
Fig. 1. Schematic diagram of the electrochemical cell. (1) Working electrode, (2) reference electrode, (3) gas chamber, (4) electrolyte chamber, (5) counter electrode.

3. Results

Figure 3 presents the steady state cathodic and anodic current–potential curves in the presence and absence of NOx. It can be seen that the reduction of the nitrogen oxides on the active carbon catalysed with CoPc starts at potentials more negative than + 350 mV (HE), while the electrochemical oxidation starts at potentials more positive than + 870 mV (HE). It can also be concluded that the rate of these two processes does not depend on the electrolyte concentration.

Previous investigations showed that the electro-catalytic oxidation of sulphur dioxide by atmospheric oxygen on a catalyst — active carbon + CoPc — proceeds in the potential range + 550–+ 700 mV (HE) [1], whereas, as seen from the present results, nitrogen oxides do not undergo electrochemical changes.

However, it was necessary to investigate the two partial reactions on which the ELCOX method is based — oxygen reduction and sulphur dioxide oxidation in the presence of NOx.

Figure 4 shows the steady state current–potential curves for oxygen reduction in the presence and absence
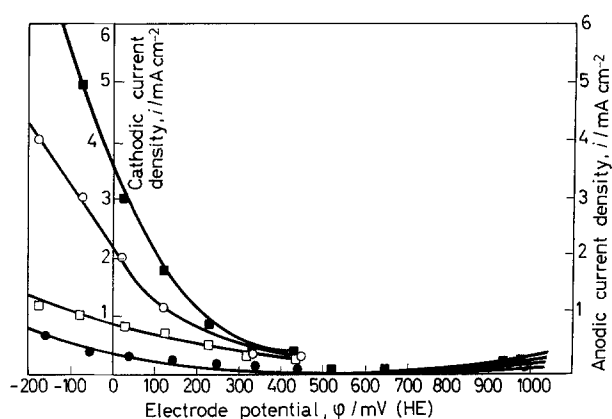

Fig. 3. Cathodic and anodic current–potential curves of gas-diffusion electrodes catalysed with CoPc, in presence and absence of NOx. (●) Ar; 0.5 M H_2SO_4, (□) Ar; 4.5 M H_2SO_4, (○) Ar + 1000 p.p.m. NOx; 0.5 M H_2SO_4 and (■) Ar + 1000 p.p.m. NOx; 4.5 M H_2SO_4.

of NOx. It is clearly seen that the presence of NOx in the gas mixture leads to a remarkable decrease of the steady state current density. Moreover, with the shift to more negative potentials at a fixed current density, the differences between the two curves increase. This result combined with the data for the electrochemical behaviour of NOx (Fig. 3) gives reason to assume that in the potential range studied (+ 400–+ 850 mV (HE)) NOx are adsorbed on the catalyst surface, whereby they block part of the active centres taking part in the oxygen reduction. It is evident that the number of blocked centres is dependent on the potential.

The data given in Fig. 5 support this assumption. Together with the current-potential characteristics of Fig. 4, it presents two additional curves. One was taken after the electrode had operated in presence of NOx. The other was obtained after the electrode had operated in gas mixture containing NOx and was subsequently washed with distilled water. It can be clearly seen that the electrode recovered its initial activity immediately after being washed with dis-
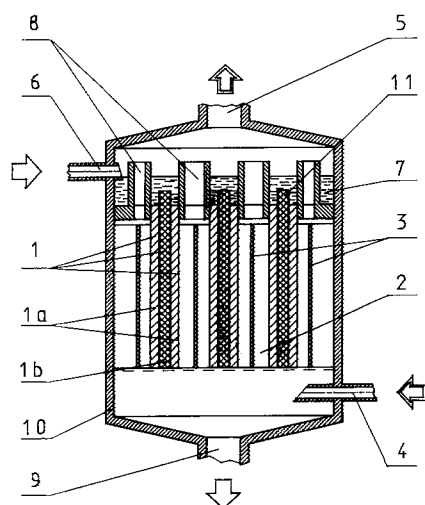

Fig. 2. Cross-section of a test column for desulphurization of gas mixtures containing sulphur dioxide. (1) catalytic sheets: a — catalyst and b — polyester felt cloth, (2) gas chamber, (3) separator, (4) gas mixture inlet, (5) gas mixture outlet, (6) H_2SO_4 solution inlet, (7) tank, (8) gas chamber outlet, (9) H_2SO_4 solution outlet, (10) casing, (11) catalytic sheet ends.
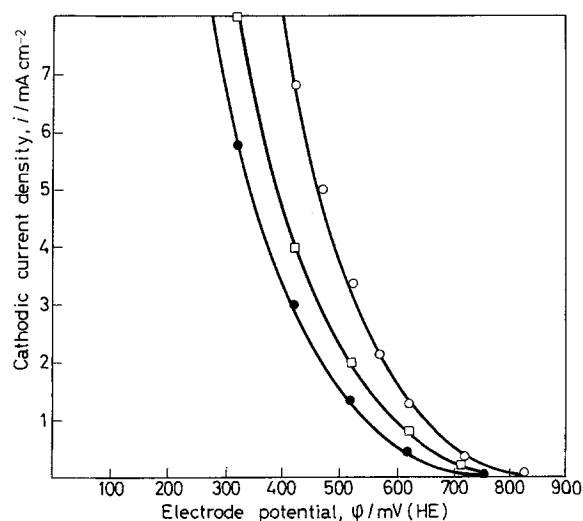

Fig. 4. Current–potential curves of a gas-diffusion electrode catalysed with CoPc, taken during oxygen reduction in presence and absence of NOx. (○) O_2(air); 0.5 M H_2SO_4, (●) O_2(air) + 1000 p.p.m. NOx; 0.5 M H_2SO_4 and (□) O_2(air) + 1000 p.p.m. NOx; 4.5 M H_2SO_4.
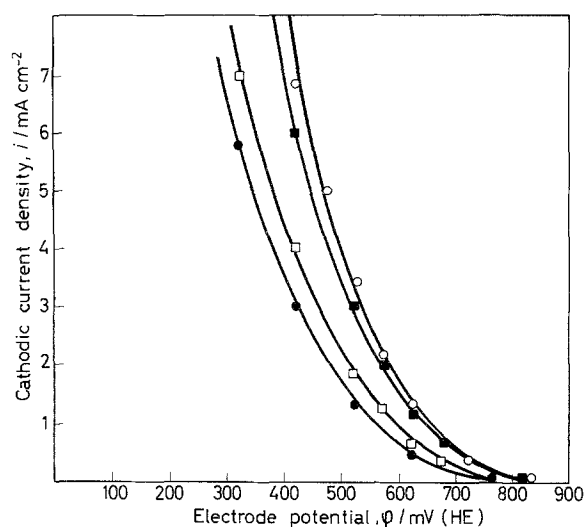
Fig. 5. Current–potential curves of a gas-diffusion electrode catalysed with CoPc, taken during oxygen reduction under various conditions. (O) O$_2$(air); 0.5 M H$_2$SO$_4$, (●) O$_2$(air) + 1000 p.p.m. NOx; 0.5 M H$_2$SO$_4$, (□) O$_2$(air), after operation in presence of NOx; 0.5 M H$_2$SO$_4$ and (■) O$_2$(air), after operation in presence of NOx and washing with distilled water; 0.5 M H$_2$SO$_4$.

Fig. 7. Change of NOx concentration at test column outlet at gas flow rate (air + 1100 p.p.m. NOx) of 100 dm^3 h^{-1}.

tilled water. The experimental data show that physical adsorption takes place in this case. Since both nitrate and nitrite ions were present in the electrolyte, it remained an open question whether they or the nitrogen oxides blocked the catalyst surface. To elucidate this matter, the following experiments were performed:

(i) Current–potential characteristics were measured on gas-diffusion electrodes in the presence of air in pure electrolyte and in electrolyte containing nitrate and nitrite ions. As can be seen from Fig. 6 the two current–potential curves do not differ.

(ii) NOx adsorption on the catalyst investigated was measured. The experiment was performed with 2 g dry hydrophobic catalyst placed in a tube supplied with an inlet and outlet. A gas mixture consisting of air and NOx (1100–1200 p.p.m.) was blown through the tube at a flow rate of 100 dm^3 h^{-1}. Figure 7 presents the

change in outlet NOx concentration as a function of time. It can be seen that after 30 min operation the catalyst virtually ceases to adsorb NOx. Calculation shows that under these conditions 1 g catalyst adsorbs about 7.5 cm^2 nitrogen oxides. A rough estimate based on the mean NOx molecule radius (1.2–2.5 A) [7] and the active carbon surface area (600 m^2 g^{-1}) indicates that the gas adsorbed can cover as much as 2–3% of this area, which actually consitutes a very small part of it. However, it must be taken into account that the active centres on the carbon surface are formed as a result of doping with 10 wt % CoPc.

On the basis of the results obtained from these experiments it can be concluded that the partial blocking of the catalyst active centres is due primarily to adsorption of the nitrogen oxides.

Figure 8 presents the steady state current-potential curves taken during SO$_2$ oxidation in the presence and absence of NOx. Owing to the low SO$_2$ concentration in the gas mixture both sets of current densities are diffusion limited. It can be seen from the figure that the presence of NOx leads to a decrease in the reaction rate, which may also be inferred on the basis of the data discussed above.

When a mixture of air and SO$_2$ is fed to the gas-diffusion electrode, two reactions take place: oxygen reduction and sulphur dioxide oxidation. The criterion for the rate of the overall process will be the current measured at the intersection point of the cathodic and
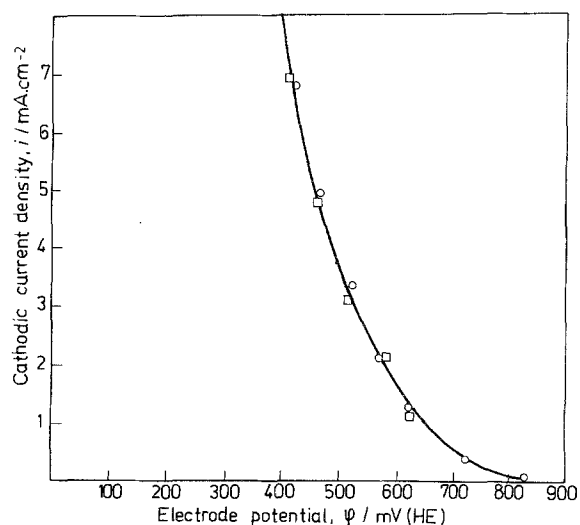

Fig. 6. Current–potential curves of a gas-diffusion electrode catalysed with CoPc, taken during oxygen reduction. (O) 0.5 M H$_4$SO$_4$ and (□) 0.5 M H$_2$SO$_4$ containing 2 × 10^{-2} M NO$_2$ and 10^{-3} M NO$_3$.
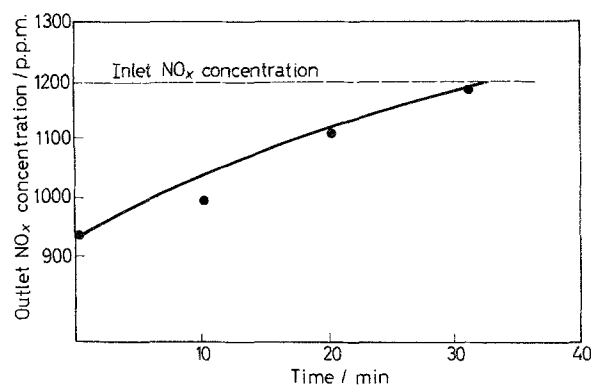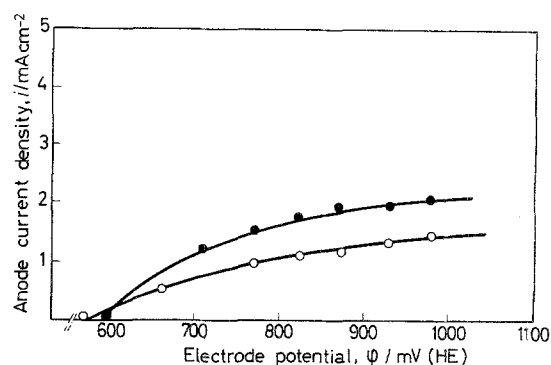

Fig. 8. Current–potential curves of a gas-diffusion electrode catalysed with CoPc, taken during sulphur dioxide oxidation in absence and presence of NOx. (●) Ar + 2000 p.p.m. SO$_2$; 0.5 M H$_2$SO$_4$ and (O) Ar + 2000 p.p.m. SO$_2$ + 1000 p.p.m. NOx; 0.5 M H$_2$SO$_4$.
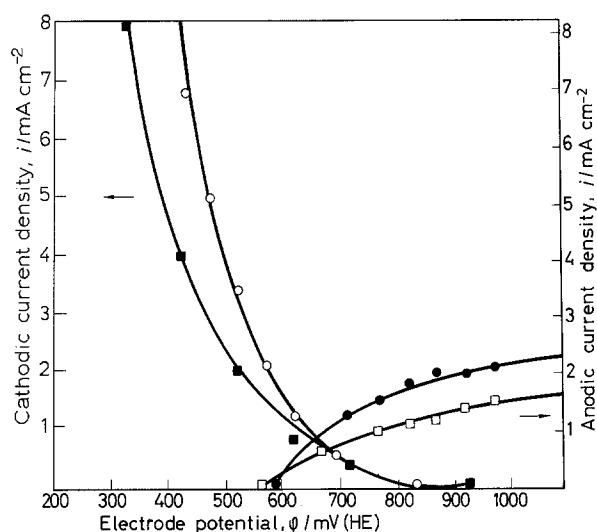
Fig. 9. Current–potential curves of a gas-diffusion electrode catalysed with CoPc, taken during sulphur dioxide oxidation in absence and presence of NOx. (O) O_2(air); 0.5 M H_2SO_4, (■) O_2(air) + 1000 p.p.m. NOx; 0.5 M H_2SO_4, (●) Ar + 2000 p.p.m. SO_2; 0.5 M H_2SO_4 and (□) Ar + 2000 p.p.m. SO_2 + 1000 p.p.m. NOx; 0.5 M H_2SO_4.

anodic curves [1]. Figure 9 compares the current–potential curves of the two partial reactions in the absence and presence of NOx. It can be clearly seen that in the presence of NOx oxides in the gas mixture the current at the intersection point decreases by 30–40%. Correspondingly, this should lead to a
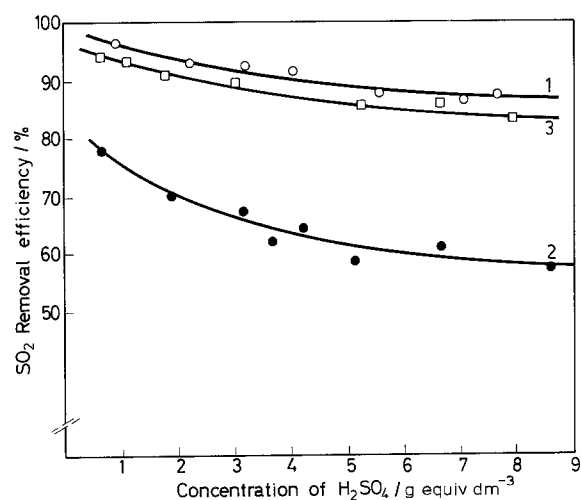

Fig. 10. Sulphur dioxide removal efficiency of a test column with 1.5 dm³ working volume at gas flow rate of 250 dm³ h⁻¹. (O) air + 2000 p.p.m. SO_2, (●) air + 2000 p.p.m. SO_2 + 1000 p.p.m. NOx and (□) air + 2000 p.p.m. SO_2 after washing the catalytic sheets with water.

proportional decrease in the SO_2 removal efficiency for gas mixtures containing both SO_2 and NOx.

To examine this assumption based on the data presented above, measurements were performed in a test column for SO_2 removal (Fig. 2). The dependence of the removal efficiency on sulphuric acid concentration is shown in Fig. 10. The curves presented were taken in the following sequence:

Curve 1 — gas mixture air + SO_2
Curve 2 — gas mixture air + SO_2 + NOx
Curve 3 — gas mixture air + SO_2

It should be noted that after each measurement the catalytic sheets were washed repeatedly with water. It can be seen from the figure that the presence of NOx actually leads to a 30–40% decrease in the SO_2 removal efficiency. Another effect observed during the electrochemical measurements also occurred: after washing the NOx are removed and the catalyst activity with respect to the SO_2 oxidation was restored.

It can be concluded that NOx adsorb on some of the active centres and partially block the surface area of the catalyst (active carbon catalysed with CoPc). As a result of this geometric effect the catalyst activity decreases by 30–40%. This should be taken into account in the design of ELCOX installations for desulphurization of gases containing NOx. To obtain the desired removal efficiency under these conditions, it is necessary to construct installations with about 30% larger size.

Acknowledgement

References

[1]   T. Vitanov, E. Budevski, I. Nikolov, K. Petrov, V. Naidenov and Ch. Christov, I. Chem. E. Symposium Series, No. 116, p. 251.
[2]   Bulgarian Patent No. 79 220 (7 April 1987).
[3]   L. J. J. Janssen, M. M. J. Pietrerse and E. Barendrecht, Electrochim. Acta 22 (1980) 10.
[4]   I. Paseka and J. Vonkova, ibid. 25 (1980) 10.
[5]   H. Ebert, R. Parsons, G. Ritzoulin and T. Van der Noot, J. Electroanal. Chem. 264 (1989) 181.
[6]   I. Iliev, S. Gamburtsev, A. Kaisheva, E. Vakanova, I. Mukhovski and E. Budevski, Dept. Chem. Bulg. Acad Sci. 7 (1974) 223.
[7]   H. Gmelins, Hanbuch der Anorganischen Chemie, Teil 4, pp. 689, 787 and 821.