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Electrochemical reduction of O_2 and NO on Ni, Pt and Au

K. K. Hansen

Abstract The electrochemical reduction of oxygen and nitric oxide was studied using cyclic voltammetry on point electrodes of Ni, Pt and Au in the temperature range 400–600 °C. All the materials were more active towards the reduction of oxygen than towards the reduction of nitric oxide, except Pt at 400 °C. As a general trend it was observed that the activity of the materials towards the reduction of oxygen increases more than the activity of the materials towards the reduction of nitric oxide with increasing temperature. The Ni wire was covered with a layer of NiO. The NiO layer inhibits the reduction of both nitric oxide and oxygen. No sign of the formation of an oxide layer on the platinum and gold wires was observed. Pt was the most active electrode material towards the reduction of nitric oxide. Au showed almost no activity towards the reduction of nitric oxide, but Au was active towards the reduction of oxygen. This implies that the triple-phase boundary (3PB) catalyses the reduction of oxygen but not the reduction of nitric oxide, as Au is a catalytic inactive metal. All the materials were more active towards oxidation than towards reduction that is evolution of oxygen or oxidation of nitric oxide to nitrogen dioxide was more pronounced than the reduction reactions.

Keywords Gold · Platinum · Nickel · Oxygen · Nitric oxide · Reduction

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1 Introduction

Removal of NO_x from exhaust gasses is difficult when the exhaust gas contains excess oxygen. Several methods are under development, among them the electrochemical reduction of NO_x. The main problem with this method is limited selectivity towards the reduction of NO_x leading to a high current consumption [1]. The activity at low temperature might also be too low for practical purposes. In principle it is possible to electrochemically reduce nitric oxide in a net oxidising atmosphere, as nitric oxide is less stable than oxygen. However, only a few electrode materials are known to act a selectively as cathodes for the electrochemical reduction of nitric oxide in a net oxidising atmosphere [2–22].

With the aim of finding useful cathodes for the electrochemical reduction of NO_x in a net oxidising atmosphere the cone shaped electrode technique has been used to study the electrochemical reduction of oxygen and nitric oxide [23–29]. It has been found that only a few electrode materials have a higher activity towards the reduction of nitric oxide than towards the reduction of oxygen. Ni has been proposed as a cathode for the electrochemical reduction of NO_x in a net oxidising atmosphere [3–21]. Ni exhibits some selectivity towards the reduction of nitric oxide in a net oxidising atmosphere. Several noble metals have also been tried, among them Pt [30–34]. Pt has a higher activity towards the reduction of oxygen than towards the reduction of nitric oxide. Pt is therefore not selective towards the reduction of nitric oxide, leading to a low current efficiency.

In this study, wires of Ni, Pt and Au are studied as cathodes for the reduction of oxygen and nitric oxide using cyclic voltammetry. When a nickel wire is heated in air a layer of NiO is formed on the surface of the wire. This

oxide layer can be reduced electrochemically. When using FactSage [35] to calculate the free energy it was found that the reduction of NiO to Ni metal is placed at a potential of approximately −0.85 V versus air at 500 °C.

2 Experimental

Wires of Ni (Alfa), Pt (Umicore) and Au (Allgemeine Gold und Silberscheideanstalt) were used as received from the suppliers. The wires were placed in a two atmosphere set-up with air as a reference gas [24]. Approximately 60 g of weight (approximately 60 MPa) was put on top of the wires. As a counter/reference electrode silver (added as silver paste, Engelhard) was used. The counter/reference electrode was large in size compared with the contact of the cone shaped electrode. As electrolyte a yttria stabilised zirconia (YSZ) tube (Vesuvius) with one end closed was used. The top of the YSZ tube was polished before use. The working electrode chamber was flushed with either air or 1% nitric oxide in argon (Hede Nielsen), whereas the counter/reference electrode chamber was flushed with air. The set-up with the wires was then heated in air to 600 °C, before recording the cyclic voltammograms. The cyclic voltammetry was performed using a Gamry Femtostat potentiostat. The measurements were done at temperatures of 600, 500 and 400 °C. Sweep rates of 1 and 10 mV s^{-1} were used throughout. The potential window spanned was either 0.2 to −0.8 V versus air or (in the case of Ni) 0.2 to −1.5 V versus air (to make sure that the reduction of NiO to Ni is covered). The wires were equilibrated at open circuit voltage (OCV) in both atmospheres before recording the voltammograms. Electrochemical impedance spectroscopy (also using the Gamry instrument) was recorded at open circuit voltage to determine the series resistance (to find the contact area of the cone shaped electrodes using Newman's formula). The EIS measurements were done at the frequency interval 300.000–0.05 Hz with 10 points measured at each decade, and an amplitude of 25 mV. Newman's formula is [36]:

$$r = \frac{1}{4R_s\sigma^*},\qquad(1)$$

where r is the radius of the contact between the electrode and the electrolyte. The specific conductivity of the electrolyte (YSZ), σ^*, was taken from [37]. R_s is the intercept with the real axis in the impedance plot at high frequency.

3 Results and discussion

The voltammograms recorded in air and in the nitric oxide containing atmosphere at 500 °C on the nickel wire can be
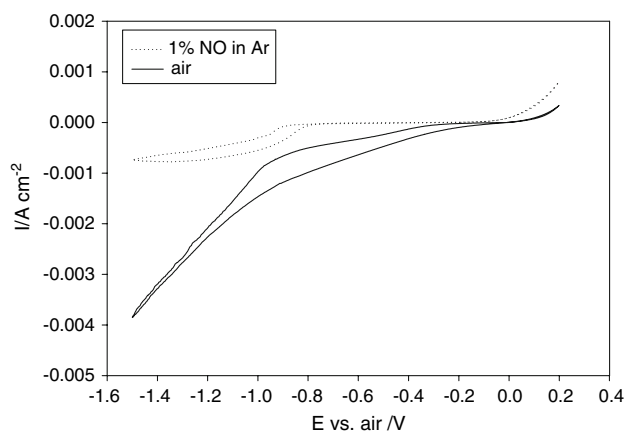

Fig. 1 Plot of the reduction nitric oxide and oxygen on a Ni/NiO electrode investigated using cyclic voltammetry at temperature of 500 °C

found in Fig. 1. In air an anodic current (from oxygen evolution) is observed at potentials above approximately the open circuit voltage (0 V versus air). Cathodic currents are observed below the open circuit voltage in air. In the nitric oxide containing atmosphere cathodic current are only observed at potentials below approximately −0.9 V versus air. This indicates that NiO has no catalytic activity towards the reduction of nitric oxide. −0.9 V versus air is just below the potential of the reduction of NiO to nickel metal. Nickel metal is therefore active towards the reduction of nitric oxide. A large inductive hysteresis upon reversal of the scan direction is observed in the cathodic region in both atmospheres. This indicates that nickel metal is more active towards both the reduction of oxygen and nitric oxide than NiO. That the activity of NiO is low towards the reduction of oxygen is in agreement with an earlier study of an electrode system containing NiO [38]. It is also observed that the activity towards the reduction of nitric oxide is lower than the activity of the NiO/Ni electrode towards the reduction of oxygen. This is in contrast to what is found in the literature. However, different configurations are used in this study and in the literature, where the Ni/NiO cathode was covered by a layer of electrolyte powder [10]. According to the authors this enhances the bonding of nitric oxide to the electrode surface. It should also be noted that nitric oxide is bound more strongly to Ni metal than oxygen [39]. In a mixture nitric oxide and oxygen will compete for the active sites. If nitric oxide is bound more strongly to the electrode than oxygen, the electrode may exhibit some selectivity towards the reduction of nitric oxide, even if the concentration of oxygen is higher than the concentration of nitric oxide. Some care should therefore be taken when making conclusions on data measured on cones in atmospheres containing only one gaseous component. However, nickel metal is more active towards the electrochemical reduction of oxygen

Table 1 The OCV in 1% nitric oxide in argon at a temperature of 500 °C for the materials Ni, Pt and Au

Material	OCV in 1% NO in Ar
Ni/NiO	−0.21 V versus air
Pt	−0.14 V versus air
Au	−0.23 V versus air

than towards the electrochemical reduction of nitric oxide as shown in this study. The OCV in the nitric oxide containing atmosphere is very low, approximately −0.21 V versus air. This is lower than expected for the reduction of nitric oxide to nitrogen. Using FactSage [35] the potential for the reduction of nitric oxide to nitrogen can be calculated as approximately 0.35 V versus air. That the reduction of nitric oxide is initiated at much lower potentials can be explained due to a mixed potential. At the open circuit potential three reactions occur, the oxidation of nitric oxide to nitrogen dioxide, evolution of oxygen and reduction of nitric oxide to nitrogen. This implies that the reduction of nitric oxide is inhibited by the evolution of oxygen and the oxidation of nitric oxide to nitrogen dioxide. Similar situations are found for the two other electrode materials investigated in this study. However, the OCV differs for the three materials (Table 1). This shows that the three materials have very different catalytic properties.

The behaviour of the platinum wire is markedly different from that of the nickel wire in both atmospheres, as seen in Fig. 2, where voltammograms recorded in air or the nitric oxide containing atmosphere at 500 °C are plotted. Anodic currents are found above the OCV in air (approximately 0 V versus air). As for the Ni/NiO electrode system the OCV is lower in the nitric oxide containing atmosphere than in air. The OCV in nitric oxide containing atmosphere is approximately −0.14 V versus air (see Table 1). Above the OCV in the nitric oxide a cathodic current is observed.
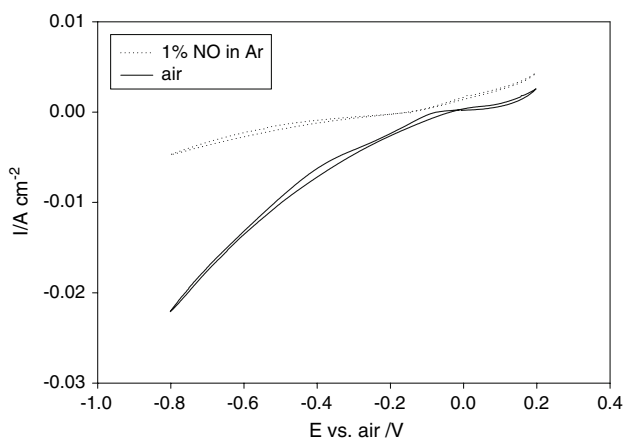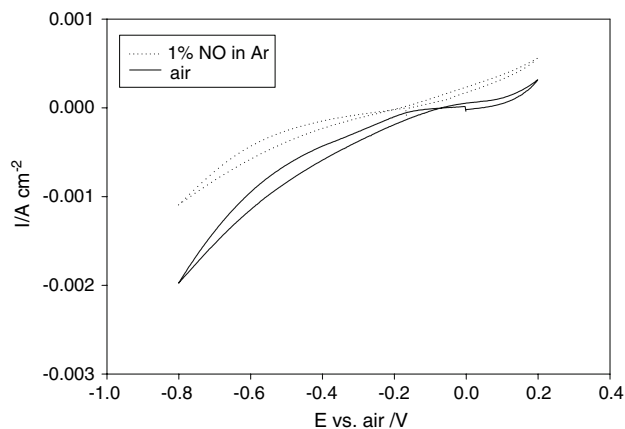

Fig. 3 Plot of the electrochemical behaviour of a Pt wire at 400 °C in either air or a nitric oxide containing atmosphere

The activity of the platinum wire is higher towards the reduction of oxygen than towards the reduction of nitric oxide at a temperature of 500 °C. This is even more marked at 600 °C (see Fig. 3). In Fig. 4 the cathodic currents are almost the same in the two atmospheres, showing that the activity towards the reduction of nitric oxide is higher than the activity towards the reduction of oxygen at this temperature. That the activity of the electrodes increases more for the reduction of oxygen than for the reduction of nitric oxide with increasing temperature is a general trend for all the materials investigated in this study. To obtain an energy efficient cell the reduction of nitric oxide should therefore be performed at low temperature.

Voltammograms recorded on the Au wire at 500 °C in air or 1% nitric oxide in argon are shown in Fig. 5. In air anodic currents are found above the OCV (approximately 0 V versus air), and cathodic currents are found below the OCV. In the nitric oxide containing atmosphere almost no activity is seen towards the reduction of nitric oxide. The Au electrode is therefore much more active towards the
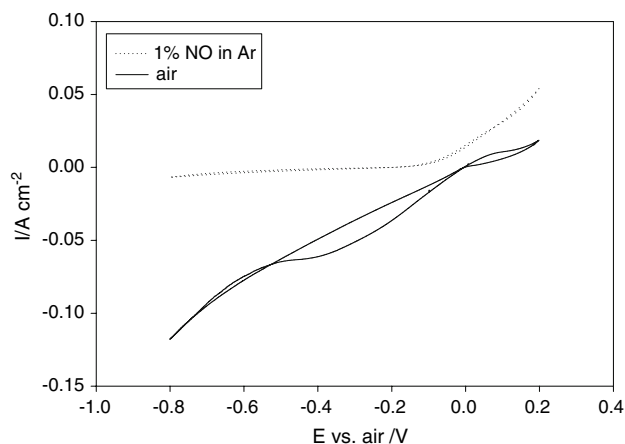

Fig. 2 Plot of the reduction of nitric oxide and oxygen on a Pt electrode at 500 °C studied by the use of cyclic voltammetry

Fig. 4 Plot of a Pt wire in an atmosphere containing nitric oxide or air at 600 °C studied by the use of cyclic voltammetry
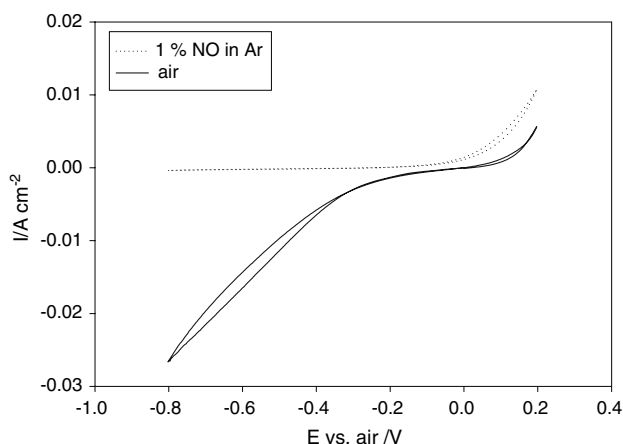
Fig. 5 Cyclic voltammograms recorded on an Au wire in either 1% nitric oxide in argon or in air at 500 °C

reduction of oxygen than towards the reduction of nitric oxide. This is observed at all temperatures investigated. This indicates the following. Gold is generally believed to be a catalytic inactive material. When a catalytic inactive material is used as a cathode, nitric oxide cannot be reduced. However, the reduction of oxygen proceeds at a measurable rate even though the cathode material is catalytic inactive. This indicates that the triple-phase boundary catalyses the electrochemical reduction of oxygen but not the electrochemical reduction of nitric oxide. This also shows that the reduction of oxygen will always be possible when an electronic conducting electrode is in contact with an ionic conducting electrolyte, whereas the reduction of nitric oxide only will be possible when an electrode material with suitable catalytic properties is used.

This, together with the information that the OCV in the nitric oxide containing atmosphere always lay below the OCV in air, means that the reduction of nitric oxide will always be carried out along with the reduction of oxygen. The reduction of oxygen cannot be totally inhibited. This also shows that the size of the triple-phase boundary must be optimised, not just maximised. Similar conclusions have been drawn in the literature (Hansen, in preparation).

4 Conclusion

Oxygen and nitric oxide can be reduced at electrodes of NiO/Ni, Pt and Au. The most active electrode for the reduction of nitric oxide is Pt. However, almost no activity of gold towards the reduction of nitric oxide was found at all temperatures. The reduction of nitric oxide is inhibited by oxygen evolution and nitrogen dioxide formation. All the electrodes are more active towards the reduction of oxygen than towards the reduction of nitric oxide except Pt at 400 °C. The surface layer of NiO inhibits the reduction

of oxygen and nitric oxide. Ni metal is also more active towards the reduction of oxygen than towards the reduction of nitric oxide. This study indicates that the triple-phase boundary catalyses the reduction of oxygen but not the reduction of nitric oxide. This means that the size of the triple-phase boundary must be optimised, not just maximized. As a general trend it is found that the electrochemical reduction of oxygen is more thermally activated than the electrochemical reduction of nitric oxide. It is therefore beneficial to run the reaction at the lowest possible temperature. However, at low temperature the activity is lower than at high temperature. An optimum operating temperature must therefore be found as a compromise between the two effects.

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