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Electrochemical reduction of NO and O_2 on Cu/CuO

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Abstract

The electrochemical reduction of NO and O_2 on a Cu-point electrode covered with a surface layer of CuO is investigated in an electrochemical cell with a gadolinium doped cerium oxide oxygen ion conducting electrolyte in the temperature interval 300–500 °C. It is shown that the reduction of NO on CuO is possible at a lower overvoltage than it is in the case of the reduction of O_2. The results indicate that the reduction of NO on CuO is not inhibited in the presence of O_2 and that the reduction of NO can be selectively performed on a CuO-electrode.

1. Introduction

NO_x (NO and NO_2) is one of the main polluting agents from internal combustion processes. At high temperature and pressure NO is formed mainly from the reaction between N_2 and O_2 according to the Zeldovich mechanism [1]:

$$O_2 \rightarrow 2\,O \tag{1}$$

$$N_2 + O \rightarrow NO + N \tag{2}$$

$$N + O_2 \rightarrow NO + O \tag{3}$$

with the overall rate equation

$$\frac{d[NO]}{dt} = 9 \times 10^{14}\,[O_2]^{0.5} \times [N_2] \exp\left(\frac{-315.6\ \text{kJ}}{RT}\right) \tag{4}$$

NO is known to give rise to acid rain (due to formation of HNO_3) and NO is a greenhouse gas. NO is less harmful than NO_2 but like CO, NO attaches to haemoglobin, to form nitroso-haemoglobin, and reduces oxygen transport efficiently [2]. In air and sunlight NO reacts rapidly with O_2 under the formation of NO_2. NO_2 is an irritant and gives rise to pulmonary oedema [3].

In the traditional three-way catalytic converter the reduction of NO_x is possible only at near stochiometric conditions and the three-way catalytic converter is not feasible for NO_x-reduction under lean conditions such as encountered in exhaust gases from diesel engines and lean burn Otto-engines. Various systems are under development for NO_x-reduction under lean conditions, see [4] for a recent review. The one gaining the most attention is the system based on a selective catalytic reactor (SCR). In a SCR the reduction of NO_x are performed by adding a reducing agent, either ammonia, urea or a hydrocarbon to the exhaust gas. The NO_x and the reducing agent then react on a catalyst, that is, Cu–ZSM (zeolite synthetic by Mobil) producing water and elemental nitrogen. Two major problems exist with the SCR solution; the storage of the reducing agent and problems with leakage of the added reducing agent (often called slip).

To avoid problems with storage and slip of the reducing agent, electrochemical reduction of NO_x is a potentially useful method. In electrochemical NO_x-removal, first suggested by Pancharatnam et al. [5], electrons are used directly as a reducing agent. Electrochemical reduction of NO_x is potentially feasible even for use under lean conditions. This is best illustrated using Figure 1. As NO (and NO_2) is less stable than O_2 the energy level of the antibonding orbitals of NO is placed at a lower energy level than the antibonding orbitals of O_2. By adjusting the potential such that the valence electrons of the electrode material are placed at an energy level in between that of the antibonding orbitals of NO and O_2, only NO will be reduced. For comparison, the standard reduction potential at 323 °C is 1.55 V for NO and 1.11 V for O_2. To benefit from this, the electrode should have a low overpotential towards NO-reduction.

Some investigations have already been undertaken using metal electrodes such as Pd [6], Pt [5, 7], Ag [8] and Ir [9] and a yttrium stabilized zirconium oxide oxygen

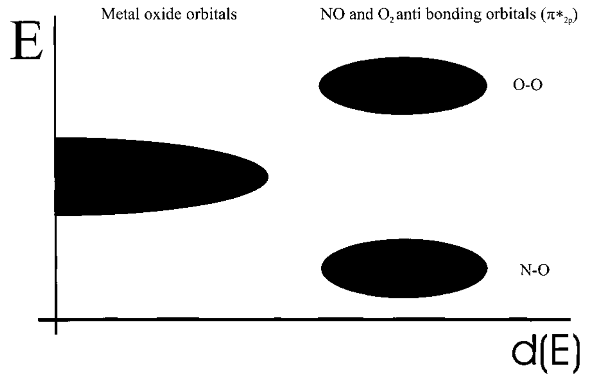

Fig. 1. Schematic picture of the energy level of the valence electrons of a metal oxide and the antibonding orbitals of NO and O_2.

ion conducting electrolyte (YSZ). Recently the oxide RuO_2 has also been suggested as a candidate for electrochemical NO_x-removal [10]. Ru is however highly poisonous and forms volatile higher oxides (RuO_3 and RuO_4).

The systems so far investigated have all had the disadvantage of the need for high temperature, due to the low ionic conductivity of the YSZ-electrolyte at moderate temperature (300–500 °C), and a low current efficiency for the NO-conversion due to parallel O_2-reduction at the cathode. For practical purposes a system working around 300 °C with a high current efficiency is necessary.

The low ionic conductivity of YSZ at moderate temperatures can be overcome by the use of an ionic conductor with a higher ionic conductivity such as gadolinium doped cerium oxide (CGO). To achieve a high current efficiency it is necessary to use a NO_x-selective electrode to avoid simultaneous reduction of O_2. The study of electrode kinetics in a system based on an oxygen ion conducting electrolyte is, however, often troublesome due to the use of porous electrodes. Porous electrodes add geometrical complications such as current dependent reaction zones and current pathways [11]. One way to overcome some of the problems is to use cone shaped (or point) electrodes, as suggested by Fabry and Kleitz [12], see Figure 2. The disadvantage of using cone shaped electrodes is that only a small electrode area is available and the magnitude of the current will be limited. This makes analysis of changes in the gas phase composition difficult, and one has to rely on electrochemistry alone.

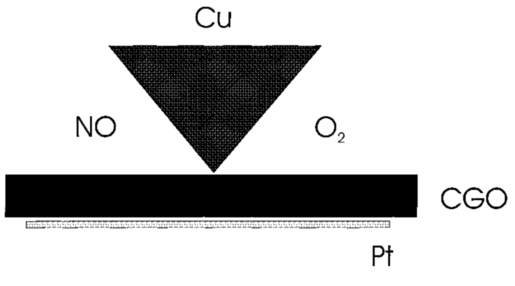

Fig. 2. Cone (or point) electrode set-up.

In this study the electrochemical reduction of NO and O_2 is investigated on a Cu-point electrode by the use of cyclic voltammetry. Cu and Cu-compounds are some of the main components in catalysts used for removal of NO_x under net oxidizing conditions.

2. Experimental details

2.1. *CGO10*

A 10% gadolinium doped cerium oxide (CGO10, specific surface area 20 $m^2\,g^{-1}$, Rhodia) was used as-received. For the fabrication of dense pellets the CGO10-powder was ball milled in a mixture of ethanol, stearic acid and glycerine for 20 h. The CGO10-powder was then pressed in a die and sintered at 1500 °C for 3 h. Before use the pellets were polished using a SiC-paper (Struers, grade 500). The density of the sintered pellets were determined using the archimedes method.

2.2. *Thermogravimetry*

Thermogravimetry (TG) measurements were performed on a Setaram TG 92-12 thermo balance. Cu-bronze (BDH, AR, for organic synthesis, max. 0.3% grease) and CuO (Merck, AR) was used as Cu and CuO sources, respectively. For the measurements, around 30 mg of powder was used. Measurements in N_2 (99.99+), 50% O_2 in N_2 and 25% NO in Ar (all from Hede Nielsen) were performed at temperatures up to 1050 °C at a heating rate of 5 °C min^{-1}. The outlet gas from the experiments in NO was analysed in situ on a Varian CH7A mass spectrometer.

2.3. *X-ray*

X-ray powder diffraction measurements were performed on the products after the TG-measurements on a Siemens D5000 X-ray powder diffractometer in the 2θ range 10° to 80° with a step size of 0.02°, with unfiltered CuK_α-radiation. Data from the ICDD file [13] was used to identify the phases present.

2.4. *Cyclic voltammetry*

For the electrochemical measurements a computerized THJ-elektronik model 2 potentiostat, a tube furnace and a special holder with separate chambers for working and reference/counter-electrodes shown in Figure 3 was used. As a Cu-point electrode a Cu-rod (Riedel de-Haën, AR) with a diameter of about 1 mm was shaped as a spike by sharpening one end of the rod on a SiC paper before use. As a reference/counter-electrode Pt-paste (Emerton) was smeared onto one side of the CGO10-pellet. The CGO10-pellet was then fixed to the inner tube of the holder with a gold gasket, by heating to 1050 °C. To avoid chemical short circuit a Pyrex seal was added to make the system gas tight. As

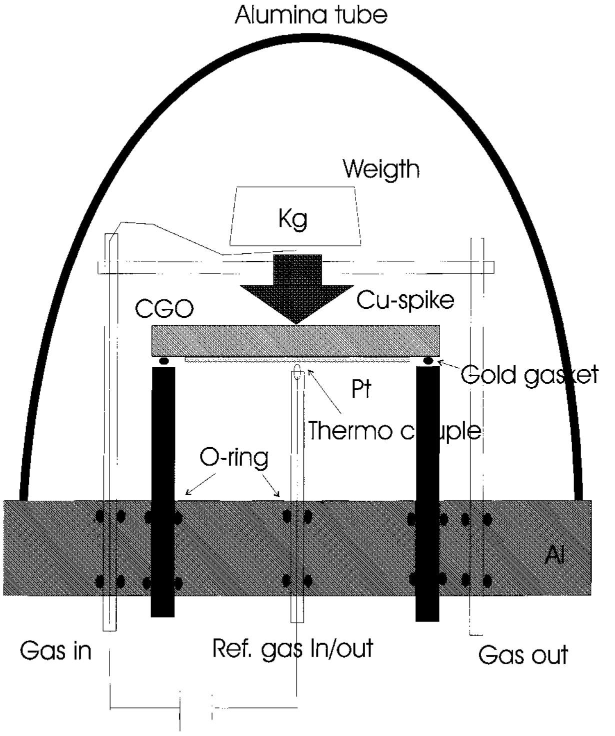

Fig. 3. Holder used for electrochemical measurements with separate gas inlet for reference electrode and working electrode chambers.

test gases, mixtures of 2% NO in N_2 and 5% O_2 in N_2 were both used as received (Hede Nielsen, with certificate). As a reference gas a 3% mixture of H_2 in Ar (Noxal 2, Hede Nielsen) was used as received. The Noxal 2 gas mixture was bubbled through a water flask equilibrated at 50 °C before entering the cell, to fix the partial pressure of water.

3. Results

3.1. *CGO10-pellets*

The relative density of the CGO10-pellets was better than 96% of the theoretical value as determined by the archimedes method using 7.22 g cm^{-3} as the theoretical density [14].

3.2. *TG and X-ray diffraction*

In Figure 4 the TG-measurements show that Cu is quickly transformed into CuO in an O_2 containing atmosphere. This was confirmed by X-ray diffraction. The transformation starts at around 200 °C and is completed at around 500 °C in an O_2 containing atmosphere. A small weight loss is observed above about 1020 °C. In the NO atmosphere the TG-measurements, Figure 4, shows that Cu starts to gain weight at temperatures above 200 °C. X-ray diffraction and mass-spectrometry shows that the main products are CuO and N_2 below 825 °C and Cu_2O and NO_2 above 825 °C. Below 300 °C N_2O was also detected. The TG-measurements in the N_2 atmosphere showed that CuO is stable to approximately 920 °C, where a large weight loss is observed.

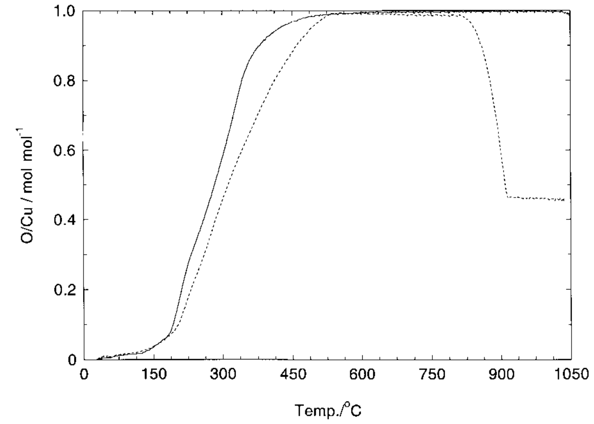

Fig. 4. Weight gain of Cu-bronze in an O_2 or a NO containing gas. Key: (——) 50% O_2 in N_2; (- - - - -) 25% NO in Ar.

3.3. *Cyclic voltammetry*

At 300 °C in the NO containing atmosphere cyclic voltammograms recorded at sweep rates 0.1, 1.0 and 10 mV s^{-1} between 1.3 V and 0.0 V after equilibration at 1.3 V for 5 min are shown in Figure 5. All potentials given in the text are vs. 3% H_2 & 8% H_2O in Ar|Pt. The intercepts with the *x*-axis depend on the sweep rate, and it is difficult to separate the anodic and cathodic reactions as no plateaux are observed at the intercept. In the cathodic sweep direction a characteristic change of slope on the 10 mV s^{-1} curve is seen at 0.48 V. In contrast with this the slope of the voltammogram is clearly decreased below 0.6 V, with the slowest sweep rate. As the maximum cathodic current decreases with decreasing sweep rate this indicates that the current to some extend has a capacitive origin. The cathodic current is numerically smaller for all sweep rates when

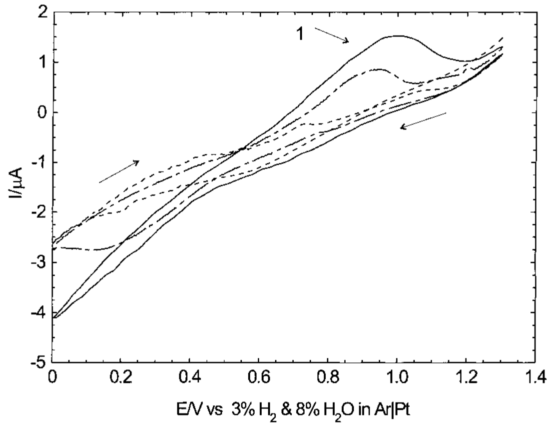

Fig. 5. Reduction of NO on Cu at 300 °C. Change of slope in the anodic scan direction at about 0.6 V and oxidation peak centred around 0.90–0.95 V is due to the redox behaviour of Cu. Arrows with number indicate oxidation/reduction process on the electrode, other arrows indicate sweep direction. (Cu electrode in 2% NO in N_2.) Key: (- - - - -) 0.1 mV s^{-1}; (– – –) 1.0 mV s^{-1}; (——) 10 mV s^{-1}.

the sweep direction is reversed. On the reverse sweep a broad anodic peak is observed at all sweep rates. The positions of the peak depends on the sweep rate, being at the lowest potential for the lowest sweep rate. Above 1.1 V the current starts to increase again showing the onset of an additional reaction.

At 400 °C the voltammograms in the NO containing atmosphere between 1.2 V to 0.0 V starting at 1.2 V is shown in Figure 6. The result is similar to those at 300 °C, except that at least three oxidation peaks are observed with the highest sweep rate.

At 500 °C, Figure 7, it becomes increasingly difficult to separate the individual contributions to the current from the anodic and cathodic reactions at potentials higher than 0.8 V, as only the sweep recorded with the highest sweep rate shows a net cathodic current above 0.8 V. Three oxidation and two reduction peaks are observed on the curve with the highest sweep rate. For the slowest sweep rates the anodic current is numerically lower at potentials above 0.9 V when the sweep direction is reversed.

To separate the ohmic and capacitive contributions to the current and to clarify the origin of the capacitive contribution, voltammograms were recorded in N_2 (to avoid interference from O_2 or NO) between 1.1 V and 0.0 V at sweep rates 1 and 10 mV s^{-1} starting at 1.1 V at 300 °C. Before the voltammograms were recorded the Cu-electrode was pre-treated in air at 300 °C. The voltammograms, plotted as C_{diff} against E to emphasize the capacitive contributions to the total current, shown in Figure 8, clearly revealed a cathodic peak with onset at 0.58 V and at least two anodic peaks, one situated at 0.52 V and a second starting at 0.7 V. The features are less clear on the sweep with the fastest sweep rate.

The voltammograms in N_2 at 400 °C and 500 °C are similar and only the voltammograms at 400 °C is shown. The voltammograms at 400 °C and 500 °C are somewhat different from those at 300 °C, see Figure 9. Three distinct peaks are seen in both the anodic and cathodic sweep directions. The capacity of the peaks is clearly influenced by the sweep rate and the capacity is highest with the lowest sweep rate. For the sweep with the lowest sweep rate the peaks are placed at $E_{cat} = 0.62$, 0.56 and 0.33 V and $E_{an} = 0.41$, 0.49 and 0.71 V.

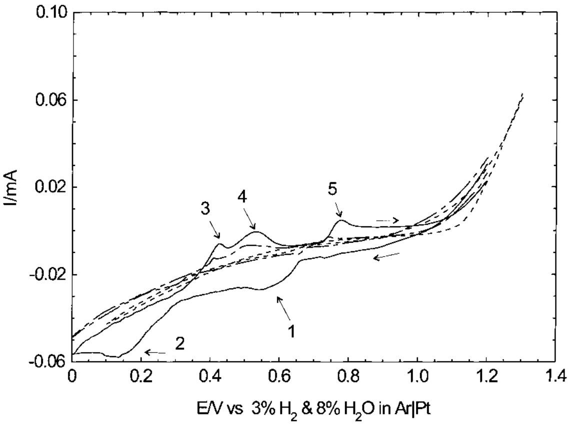

Fig. 7. Reduction of NO at 500 °C. Sweep direction indicated with arrows. Peaks labelled 1–5 are due to the reduction of CuO to Cu and the reoxidation of Cu to CuO. (Cu electrode in 2% NO in N_2.) Key: (- - - - -) 0.1 mV s^{-1}; (– - –) 1.0 mV s^{-1}; (——) 10 mV s^{-1}.

The behaviour of the Cu-electrode in an O_2 containing atmosphere at 300 °C between 1.2 V and 0.0 V, starting at 1.2 V is shown in Figure 10. In the cathodic sweep direction the electrode showed only a negligible cathodic activity above 0.8 V and only a small activity is observed above 0.6 V. Below 0.6 V the cathodic current increases significantly. It is noteworthy that, with the sweep rate 1 mV s^{-1}, the current is numerically higher when the sweep direction is reversed. A small oxidation peak is observed at 0.7 V on the sweep with the fastest sweep rate.

The electrochemical behaviour of the Cu-electrode in the O_2 containing atmosphere at 400 °C, Figure 11 is close to that observed at 300 °C and the reduction of O_2

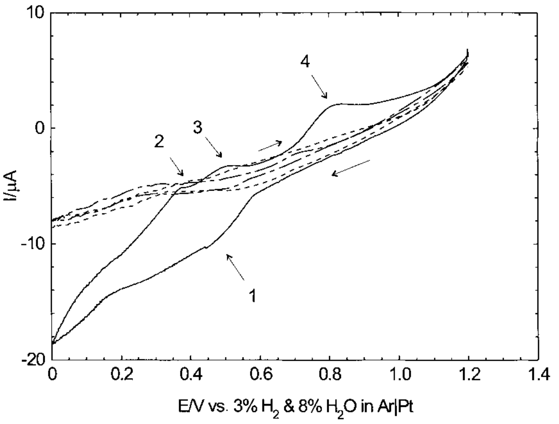

Fig. 6. Reduction of NO on a Cu-electrode at 400 °C. Peaks labelled 1–4, most easily seen on the voltammogram with the highest sweep rate, are due to the reduction/oxidation of CuO/Cu. Arrows indicate sweep direction. (Cu electrode in 2% NO in N_2.) Key: (- - - - -) 0.1 mV s^{-1}; (– - –) 1.0 mV s^{-1}; (——) 10 mV s^{-1}.

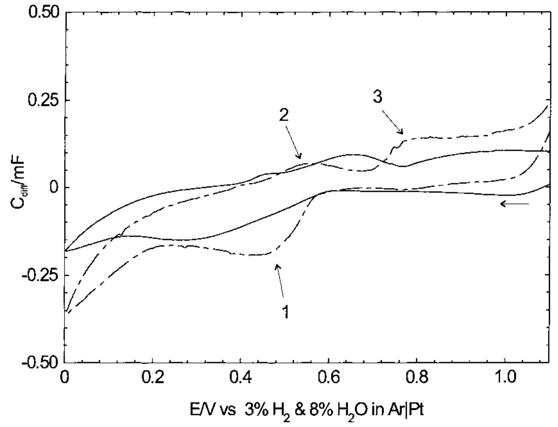

Fig. 8. A Cu-electrode pretreated in O_2 at 300 °C in N_2 at 300 °C. To emphasize the capacitive nature of the reactions taking place on the Cu-electrode the voltammograms are plotted as capacity against potential. One reduction and at least three oxidation peaks (numbered) are observed with both sweep rates. Key: (– - –) 1.0 mV s^{-1}; (——) 10 mV s^{-1}.

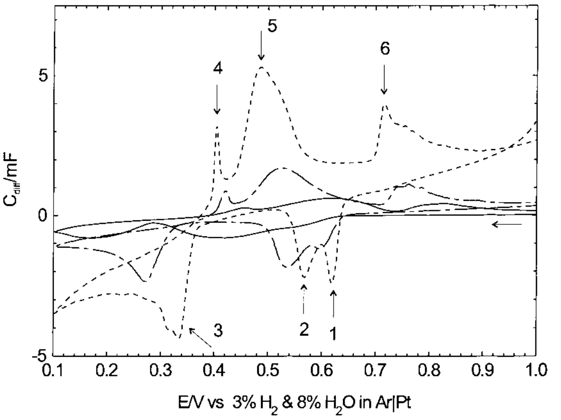

Fig. 9. A Cu-electrode with a surface layer of CuO in N_2 at 400 °C. Three distinct anodic and cathodic peaks are observed (numbered on the Figure). Sweeps recorded in N_2 do not contain any contributions from the gas phase. This helps in the elucidation of the sweeps obtained in O_2 and NO. Sweep direction indicated with arrows. Key: (- - - - -) 0.1 mV s^{-1}; (– - –) 1.0 mV s^{-1}; (——) 10 mV s^{-1}.

does not start before below 0.7 V. For all three sweep rates the cathodic current is numerically higher when the sweep direction is reversed, that is the reaction is inductive. An anodic peak is observed only with the fastest sweep rate at 0.75 V.

The voltammograms in the O_2/N_2 mixture at 500 °C on the other hand clearly reveal a plateau situated at about 1.0 to 0.8 V, and the reduction of O_2 only starts at potentials lower than 0.73 V, see Figure 12. At least two peaks are seen in both the cathodic and anodic sweep directions. The same inductive phenomenon observed at lower temperatures is also seen at 500 °C. The anodic current, above 1.05 V, is lower when the sweep direction is reversed, showing that the electrode is deactivated to some to extent when the electrode has been polarized at a low potential.

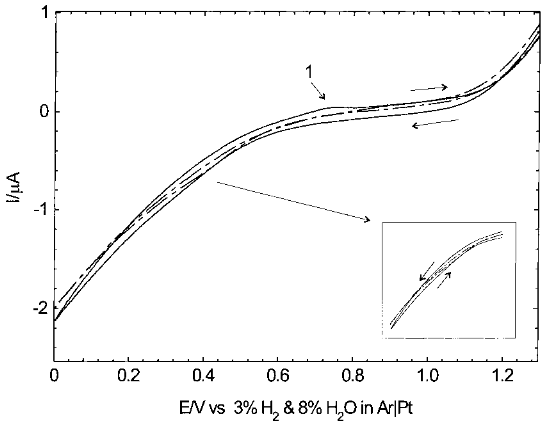

Fig. 10. Reduction of O_2 on Cu at 300 °C. Note the change of slope at 0.60 V in the negative sweep direction and the smooth oxidation peak centred at 0.75 V, marked '1', in the positive sweep direction. This is due to the reduction of CuO and the reoxidation of Cu. Positive current at potentials higher than 1.05 V is due to O_2 generation. Reduction of O_2 is inductive when the sweep rate 1 mV s^{-1} is used, as illustrated by the arrows shown in the insert. (Cu electrode in 5% O_2 in N_2.) Key: (– - –) 1.0 mV s^{-1}; (——) 10 mV s^{-1}.

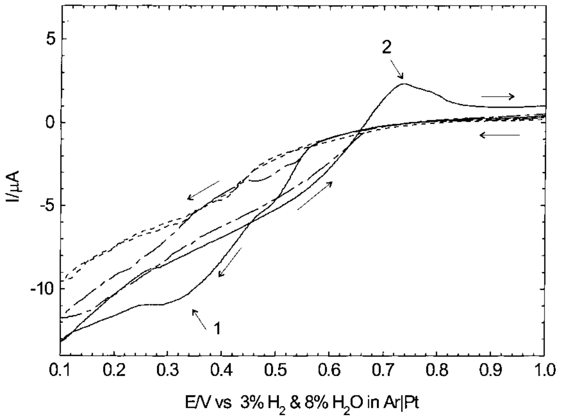

Fig. 11. A Cu-electrode at 400 °C in an O_2 atmosphere (5% O_2 in N_2). Reduction of O_2 on Cu, covered with a surface layer of CuO, is strongly inhibited and does not start before below 0.55 V, where CuO is reduced to Cu, peak labelled '1'. Current is numerically higher when sweep direction is reversed showing that the reduction of O_2 on Cu is faster than the reduction of O_2 on CuO. Arrows indicate sweep direction. Key: (- - - - -) 0.1 mV s^{-1}; (– - –) 1.0 mV s^{-1}; (——) 10 mV s^{-1}.

To obtain an indication of the effect of how the reduction of NO is altered in the presence of O_2 a sweep in a mixture of NO and O_2 (1% NO and 2.5% O_2 in N_2) was performed between 1.2 V to 0.0 V starting at 1.2 V at 400 °C. The results shown in Figure 13 look similar to the sweeps in NO atmosphere.

4. Discussion

The TG and X-ray diffraction measurements show that in an O_2 or NO containing atmosphere Cu is rapidly transformed into CuO at temperatures above 200–250 °C. In the reaction between Cu and NO below 825 °C mass-spectrometry show that N_2 is the most important gas phase product. The formation of N_2O is a well known phenomenon at low temperatures [15, 16].

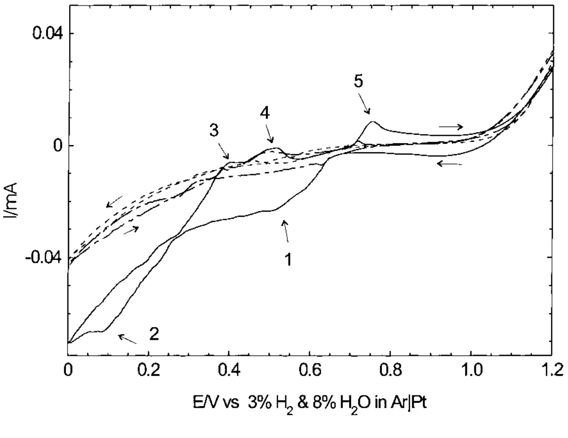

Fig. 12. At 500 °C, reduction of O_2 starts below 0.73 V, showing that reduction of O_2 is inhibited as long as the Cu-electrode contains a surface layer of CuO. Peaks labelled 1–5 are due to the reduction/oxidation of CuO/Cu. (Cu electrode in 5% O_2 in N_2.) Key: (- - - - -) 0.1 mV s^{-1}; (– - –) 1.0 mV s^{-1}; (——) 10 mV s^{-1}.

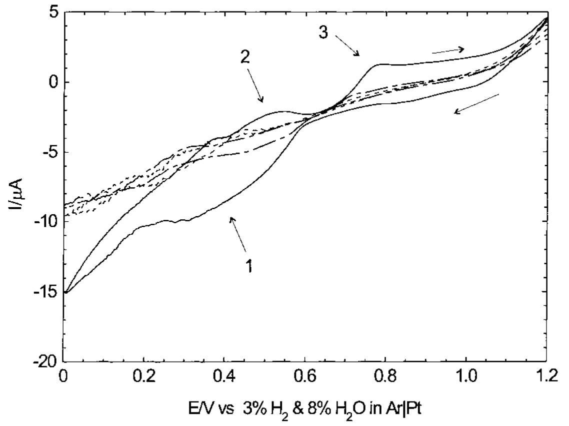

Fig. 13. Voltammograms recorded in a mixture of NO and O_2 at 400 °C. Behaviour of the Cu-electrode is similar to its behaviour when only NO is the only gas phase component, see Figure 6. (Mixture: 1% NO and 2.5% O_2 in N_2.) Key: (- - - - -) 0.1 mV s^{-1}; (– – –) 1.0 mV s^{-1}; (——) 10 mV s^{-1}.

In the NO atmosphere CuO is however reduced rapidly to Cu_2O above 825 °C under the formation of NO_2. The weight loss observed for CuO in 100% N_2 at 920 °C and in 50% O_2 at 1020 °C in N_2 is in agreement with literature data for the temperature for the transformation of CuO to Cu_2O [17]. In the temperature range of interest in this work the TG, X-ray and mass-spectrometry measurements show that the Cu-electrode will be covered with a surface layer of CuO.

The electrochemical behaviour of the Cu-electrode (pre-treated in O_2) in N_2 can then be understood from the knowledge that a surface layer of CuO is formed on Cu. At 300 °C the cathodic peak starting at 0.56 V correspond very well with the calculated value for the reduction of CuO to Cu, $E_{cat} = 0.58$ V. (The potentials are calculated using ΔG° values taken from [18].) At potentials lower than 0.56 V CuO is therefore reduced to Cu. When the sweep direction is reversed two anodic peaks are observed indicating that Cu is not oxidized directly to CuO, but that Cu most likely is oxidized first to Cu_2O and then to CuO. The anodic current seen above 1.05 V is due to the formation of O_2 and the continuing oxidation of Cu.

The behaviour in N_2 at higher temperatures is somewhat more complicated as the voltammograms reveal three distinct cathodic and anodic peaks. In addition, as is the case at 300 °C, the reaction pathway for the reduction of Cu to CuO is not just reversed when Cu is oxidized to CuO. The reduction of CuO seems to proceed both directly to Cu (peak at 0.54 V) and via the formation of Cu_2O (peak at 0.60 V). Cu_2O is then reduced to Cu at 0.33 V. This agrees well with the calculated equilibrium potentials, 0.56, 0.63, and 0.36 V. Another explanation for the oxidation of Cu must be found. The first anodic peak situated at 0.41 V may correspond to the formation of Cu_2O, in good agreement with the calculated equilibrium potential. But the second anodic peak begins before the calculated equilibrium potential for the oxidation of Cu to CuO, that is, before it is thermodynamically possible. However Kaito et al. [19] found that the mixed valence compound $Cu(\textsc{ii})_3Cu(\textsc{i})_2O_4$, with the mineral name paramelaconite, was formed by heating a Cu grid in air at 450 °C. Later Von Richthofen et al. [20] conducted a series of experiments where they, by increasing the O_2 partial pressure in the range 0–10^{-2} Pa, found that Cu_2O was formed at the lowest O_2 partial pressures, paramelaconite at intermediary O_2 partial pressures, and CuO at the highest O_2 partial pressures. In an N_2-atmosphere where the only oxygen source is the oxygen supplied to the copper electrode by electrochemical pumping it seems likely that paramelaconite could be formed. It is, therefore, suggested that the oxidation of Cu to CuO proceed via formation of a paramelaconite phase. The last anodic peak could then be the oxidation of Cu_2O to CuO. The capacity is strongly dependent on the sweep rate, being highest for the lowest sweep rate. The amount of CuO that is reduced/formed on the Cu-electrode is therefore increased when the sweep rate is decreased. Not surprisingly, the reaction rate is much increased at higher temperature.

In the O_2-containing atmosphere at 300 °C the reduction of O_2 does not start before 0.6 V. This is at about the same potential as where CuO is reduced to Cu in the N_2 atmosphere. The calculated equilibrium potential for the oxygen exchange reaction is 1.05 V and the reduction of O_2 is therefore strongly inhibited on CuO as the reduction of O_2 first proceeds at a measurable rate when CuO is reduced to Cu. Below 0.6 V the reaction, therefore, consists of two contributions, the reduction of O_2 and the reduction of CuO to Cu. When the sweep direction is reversed Cu is oxidized back to CuO at around 0.7 V. The behaviour of the Cu-electrode in the O_2 atmosphere at higher temperatures is qualitatively the same as at 300 °C. But, as the redox behaviour of the CuO/Cu system is more complicated at higher temperatures, this complicates the voltammograms recorded in the O_2 atmosphere as well. The sweeps in O_2 are best understood if one imagines a superposition of the redox behaviour of Cu on the current arising from the reduction of O_2 to oxygen anions and transport of oxygen anions through the electrolyte. The sweeps recorded in N_2 therefore help to explain the sweeps in O_2. As CuO is less stable at higher temperatures, the reduction of CuO also starts at a higher potential, therefore the reduction of O_2 is initiated at a higher potential, as at lower temperatures the voltammogram consists of two contributions, the oxidation/reduction of the Cu/CuO electrode and the reduction of O_2.

At 500 °C and the highest sweep rate a net negative current is observed in the cathodic sweep direction before the onset of the reduction of CuO. That it is observed only for the highest sweep rate indicates that the current has a capacitive origin. The current may therefore be due to double layer charging. That the current is numerically higher when the sweep direction is reversed, before Cu is oxidized to CuO, and that the reduction of O_2 starts only at significantly lower potential than the calculated equilibrium potential for the oxygen exchange reaction, when CuO is reduced to Cu, shows that the reduction of O_2 is inhibited on CuO and that the reduction of O_2 is faster on Cu than on CuO.

The interpretation of the behaviour of the Cu-electrode in the NO containing atmosphere is more complicated. At 300 °C, at potentials around the intercept with the x-axis, it is very difficult to separate the contributions from the oxygen exchange reaction, the oxidation of Cu and the reduction of NO, as no change of the slope and no plateau are observed at $I = 0$. It is therefore difficult to establish where the reduction of NO begins. At potentials lower than 0.95 V (depending on the sweep rate), however, a net negative current is observed owing to a net transport of oxygen anions away from the Cu-electrode, that is, before the reduction of CuO to Cu. It is known that CuO is catalytically active for NO-decomposition [21] and the reduction of NO is therefore possible on CuO in contrast to the reduction of O_2. As is the case in the O_2 containing atmosphere the sweeps consist of two contributions, the reduction/oxidation of CuO/Cu and the reduction of NO followed by transport of oxygen anions through the electrolyte. Some hysteresis is observed, but it is difficult to evaluate the magnitude, as several sources contribute to the total current in the voltammograms. The behaviour at 400 °C is close to that at 300 °C.

The anodic behaviour at potentials above about 1.05 V at 300 °C and 400 °C is close to being the same in the NO, O_2, or N_2 atmospheres. This indicates that NO is not oxidized to NO_2 at low temperatures, but that O_2 generation is the dominant anodic reaction.

With the highest sweep rate a net negative current is observed before the reduction of CuO begins at 500 °C, as is the case at lower temperatures. However, only a small negative current is observed before the reduction of CuO begins at the slowest sweep rates. This indicates that CuO is not a suitable electrode material for NO-reduction at temperatures above about 400 °C. Another possibility could be that more than one reaction takes place on the electrode at potentials above 0.8 V. If the oxidation of NO to NO_2 proceeds along with the reduction of NO the total current will be made up from contributions from both reactions. This makes it difficult to evaluate where the reduction of NO starts. When O_2 and NO is mixed the result is close to that observed in the NO containing gas. This indicates that O_2 is not an inhibitor toward the NO-reduction on CuO/Cu.

To summarize, the results show that the reduction of O_2 is strongly inhibited on CuO. But, as CuO is an excellent catalyst for NO-decomposition [21], the reduction of NO proceeds rapidly on CuO. The difference between Cu and other metals is that the oxide (CuO) has catalytic properties towards NO-decomposition in contrast to Pt-oxide.

For use as an electrode material a sufficient electronic conductivity is necessary, and if some oxygen ion conductivity is present this will lead to an extension of the triple phase boundary [22]. CuO is reported to be a p-type semiconductor with an electrical conductivity in the order of 0.03–0.1 S cm^{-1} in the temperature interval 300–500 °C [23], which is several orders of magnitude higher than the ionic conductivity of CGO10 in the same temperature interval [24]. No literature data has been reported on the oxygen ion conductivity of CuO. But CuO is metal deficient [25], with a fully occupied oxygen lattice, and this is normally accompanied by a low oxygen ion conductivity [26]. This problem can easily be overcome by mixing the electrode material with a small amount of electrolyte material [27].

5. Conclusion

At temperatures above 200 °C, in atmospheres containing either NO or O_2, Cu is rapidly transformed into CuO. Whereas the reduction of O_2 is inhibited on CuO this is not the case with NO. CuO could therefore be useful as a NO-selective electrode for use in electrochemical exhaust gas abatement.

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