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LETTER

Low temperature reduction of NO and O_2 on A-site deficient $(Pr_{0.6}Sr_{0.4})_{1-s}Fe_{0.8}Co_{0.2}O_{3-\delta}$ perovskites

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Introduction

At the high temperature in the combustion of fossil fuels NO_x is formed [1]. The emission of NO_x is highly unwanted as it leads to formation of smog and acid rain [2, 3]. For that reason a lot of effort has been put into lowering the emission of NO_x and several routes for lowering the NO_x emissions have been proposed [4]. When removing NO_x, from an exhaust from an engine running under lean conditions, excess oxygen in the exhaust causes difficulties. However, several routes to removal of NO_x under net oxidizing conditions exist. Among the routes the selective catalytic reduction (SCR) of NO_x has attained the most attention [5]. In the SCR process a reducing agent (typically urea) is added to exhaust gas. Urea then reacts with the NO_x on a suitable catalyst. The main disadvantage of this technique is the need of the reducing agent, which has to be stored on-board the vehicle. There is also the possibility of slip of the reduction agent. An alternative route to removal of NO_x is electrochemical reduction of the NO_x [6]. In a solid state electrochemical reactor, based on an oxide anionic conductor, the NO_x can be reduced at the cathode to nitrogen and oxide anions, as suggested by Pancharatnam et al. [7]. The oxide anions are then transported through the electrolyte, to the anode, where oxygen is formed. Like most other techniques, the presence of excess oxygen causes problems in the electrochemical removal of NO_x. Oxygen can be reduced at cathode along with nitric oxide. This leads to a low current efficiency. The key to success of electrochemical removal of NO_x is therefore the development of selective cathode materials, which has a much higher rate towards the reduction of nitric oxide than towards the reduction of oxygen. Several such cathodes have been proposed in the literature [8, 9]. The main problems with the cathodes suggested in the literature, are that they are expensive or even poisonous. If electrochemical removal of NO_x, under net oxidizing conditions, is going to be commercialized the cathodes have be of low cost. In search of such a series of A-site deficient $(Pr_{0.6}Sr_{0.4})_{1-s}Fe_{0.8}Co_{0.2}O_{3-\delta}$ perovskites ($s = 0.01$, 0.05, 0.10, 0.15, 0.20 and 0.25) were synthesized and characterized as electrode materials, towards oxygen and nitric oxide reduction, using cone-shaped electrodes and cyclic voltammetry. The use of cone-shaped electrodes is highly useful when comparing different electrode materials [10]. Several papers have already been published using the cone-shaped electrode technique to evaluate potential ceramic electrode materials for reduction of NO_x [11–14]. For perovskite-based perovskite electrodes it has been shown that the activity towards reduction of nitric oxide depends on several factors, among them redox activity and amount of oxide ion vacancies [12]. No studies of A-site deficient perovskites as cathodes for the electrochemical reduction of nitric oxide have been reported in the literature. The A-site deficient $(Pr_{0.6}Sr_{0.4})_{1-s}Fe_{0.8}Co_{0.2}O_{3-\delta}$ perovskites has already been studied as oxygen reduction cathodes at higher temperature [15]. The slightly A-site deficient $(Pr_{0.6}Sr_{0.4})_{0.95}Fe_{0.8}Co_{0.2}O_{3-\delta}$ perovskites was shown to have the highest activity towards the reduction of oxygen.

Experimental

Six A-site deficient $(Pr_{0.4}Sr_{0.6})_{1-s}Fe_{0.8}Co_{0.2}O_{3-\delta}$ perovskites, with s equal to 0.01, 0.05, 0.10, 0.15, 0.20 and 0.25

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were synthesized using the glycine-nitrate route [16]. In short aqua's solutions of the metal-nitrates were mixed in a beaker in the appropriate ratio, before glycine was added. The solutions were the heated on a hot plate until ignition. After transfer to alumina crucibles the powders were calcined at 1100 °C in air for 12 h. As metal-nitrates the following were used; $Pr(NO_3)_3{\cdot}6H_2O$ (Alfa Aesar, 99.9%), $Sr(NO_3)_2$ (Alfa Aesar, 99%), $Fe(NO_3)_3{\cdot}9H_2O$ (Alfa Aesar, 98%), and $Co(NO_3)_2{\cdot}6H_2O$ (Alfa Aesar, 99.8%). The phase purity of the powders was checked using a Stoe theta–theta diffractometer. Cylinders for fabrication of cone-shaped electrodes were made by the use of a pressing die with a diameter of 10 mm. Approximately 7 g of powder was used for fabrication of one cylinder. The cylinders were sintered at 1250 °C for 12 h in air. After sintering the cylinders were machined into cone-shaped electrodes using diamond tools. The electrochemical measurements were performed in a pseudo three-electrode set-up described elsewhere [13]. The set-up is a two atmosphere set-up with air on the counter/reference electrode side, and either air or 1% nitric oxide in argon on the working electrode side. The set-up is placed in a vertical tube furnace. As a counter/reference electrode platinum was used. The area of the platinum counter/reference electrode was many times larger than the area of the working electrode. As an electrolyte a one-end closed YSZ (yttria stabilized zirconia) tube (Vesuvius) was used. The tube was polished on the closed end, on the working electrode side, with diamond paste. The working electrode was pressed on the closed end with a weight of approximately 60 g. The measurements were performed at 200, 300 and 400 °C. At each temperature and gas composition electrochemical impedance spectroscopy (EIS) was performed at OCV (open circuit voltage). The frequency range used was 300 kHz to 50 mHz, with six points measured at each decade. As amplitude 36 mV was used throughout. The EIS measurements were used to find the contact area of the cone-shaped electrodes, using Newman's formula [17]. The conductivity of the YSZ-based electrolyte was determined using the equation given by Appel et al. [18]. Cyclic voltammograms were recorded in the potential range 0.4 to −0.8 V versus air with sweep rates of 1 and 10 mV/s at all temperatures and gas compositions. The electrodes were equilibrated at OCV before recording the voltammograms. For the electrochemical measurements a Gamry Femtostat was used.

Results

The results from powder XRD analysis has been published elsewhere [15]. The synthesized powders were found to consist of a perovskite phase, and for the more A-site deficient perovskites in addition a Co–Fe-based spinel phase, as observed for the A-site deficient $(La_{0.6}Sr_{0.4})_{1-s}Fe_{0.8}Co_{0.2}O_{3-\delta}$-based perovskites [19]. Examples of voltammograms are given in Figs. 1, 2 and 3, for the most A-site deficient perovskite $(Pr_{0.6}Sr_{0.4})_{0.75}Fe_{0.8}Co_{0.2}O_{3-\delta}$. At 200 °C the activity in the nitric oxide containing atmosphere is much higher than the activity in air. When increasing the temperature the electrodes become more active in air than in the nitric oxide containing atmosphere. This is a general trend for all the tested electrodes. In the nitric oxide atmosphere it is observed that the reduction of nitric oxide is initiated at potentials of approximately −0.2 V versus air. The current densities in air or nitric oxide are given in Table 1. The current densities are given for a potential of −0.8 V versus air. For several of the A-site deficient perovskites the activity in air at 200 °C was so low that it was not possible to make proper measurements with the Gamry Femtostat. For that reason no values are given in Table 1 for these compounds. The most active electrode in the nitric oxide containing atmosphere, at 200 and 300 °C, is the most A-site deficient perovskite. At 400 °C the activity in the nitric oxide containing atmosphere towards reduction of nitric oxide, decreases with increasing A-site deficiency. In Table 2 the maximum anodic current densities in the nitric oxide containing atmosphere at 400 °C are given as a function of A-site deficiency. The highest current density is found for the perovskite with the lowest A-site deficiency.

Discussion

The voltammograms recorded in air, shown in Figs. 1, 2 and 3, reveals that the electrodes are active towards both oxygen evolution and reduction of oxygen. At 400 °C a very large hysteresis is observed. There is also an indication of a cathodic peak at a potential of around −0.5 V versus air. This peak can have several origins. Using Factsage to calculate the potential for the reduction of Co_3O_4 to CoO gives a potential of −0.45 V versus air. This peak could therefore very well be due to the reduction of the cobalt spinel to Co(II)-oxide. Another possibility is a rate limiting chemical step in the reaction sequence. This possibility is likely as the cathodic peak not is observed in the nitric oxide containing atmosphere. If the peak observed in air is due to the reduction of the cobalt spinel, it should be visible in both air and the nitric oxide containing atmosphere. At lower temperatures this peak is not visible in the voltammograms. The activity of the tested electrode materials towards the reduction of oxygen is decreasing with increasing A-site deficiency. This could be due to loss of cobalt from the perovskite phase, when the A-site deficiency is increased. This is almost the same trend as observed at higher temperature [15]. The same

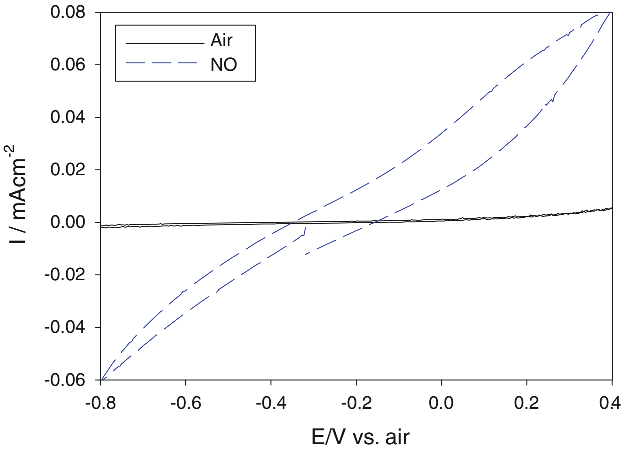

Fig. 1 Voltammograms recorded in either air or nitric oxide containing atmosphere on $(Pr_{0.6}Sr_{0.4})_{0.75}Fe_{0.8}Co_{0.2}O_{3-\delta}$ at 200 °C. The activity of the electrode is much higher in the nitric oxide containing atmosphere than in air

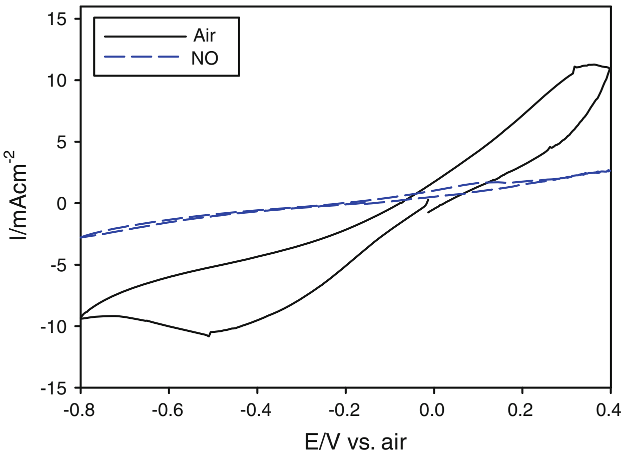

Fig. 3 Voltammograms recorded in either air or nitric oxide containing atmosphere on $(Pr_{0.6}Sr_{0.4})_{0.75}Fe_{0.8}Co_{0.2}O_{3-\delta}$ at 400 °C. The activity of the electrode is higher in air than in the nitric oxide containing atmosphere

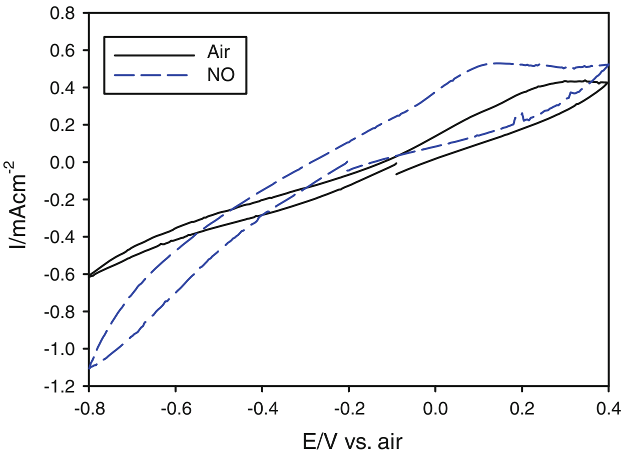

Fig. 2 Voltammograms recorded in either air or nitric oxide containing atmosphere on $(Pr_{0.6}Sr_{0.4})_{0.75}Fe_{0.8}Co_{0.2}O_{3-\delta}$ at 300 °C. The activity of the electrode is almost the same in the nitric oxide containing atmosphere and in air

trend is also observed for the reduction of nitric oxide at 400 °C, and the same argument as for the reduction of oxygen can be used. At lower temperatures the $(Pr_{0.6}Sr_{0.4})_{0.75}Fe_{0.8}Co_{0.2}O_{3-\delta}$ perovskite has the highest activity towards the reduction of nitric oxide. This is due to the fact that the $(Pr_{0.6}Sr_{0.4})_{0.75}Fe_{0.8}Co_{0.2}O_{3-\delta}$ perovskite has extremely low activation energy in the nitric oxide containing atmosphere. The reason for this is not known. It is a general trend that the reduction of oxygen has a higher activation energy than the reduction of nitric oxide. This has also been reported in the literature [11]. The potential for the initiation of the reduction of nitric oxide is much lower than the calculated value [6]. The reason for this is that the OCV is a mixed potential, determined by three reactions. The three reactions are reduction of nitric oxide, oxidation of nitric oxide to nitrogen dioxide and oxygen evolution. This has also been found for other electrode materials [6]. The oxygen evolution and oxidation of nitric oxide to nitrogen dioxide inhibits the reduction of nitric oxide. At 300 and 400 °C an anodic peak is visible in the voltammograms recorded in the nitric oxide containing atmosphere. It is speculated that this is due some sort of nitrate formation on surface of the electrode material. Such an anodic peak has also been observed for other perovskite type electrode materials [11]. The maximum anodic current densities in the nitric oxide containing atmosphere is highest for the perovskites with the lowest A-site deficiency, see Table 2. This shows that either oxidation of nitric oxide to nitrogen dioxide or oxygen evolution occurs most smoothly on this compound. For the other A-site deficient perovskites there is a small increase in the maximum anodic current density with increasing A-site deficiency until $s = 0.20$. Perhaps this is due to an increasing amount of spinel phase in the electrodes. Co–Fe Spinels have before been shown to be good electrodes for oxidation processes [14].

Conclusion

Oxygen and nitric oxide can be reduced at low temperature on A-site deficient $(Pr_{0.6}Sr_{0.4})_{1-s}Fe_{0.8}Co_{0.2}O_{3-\delta}$-based perovskites. In the nitric oxide containing atmosphere the OCV is a mixed potential determined by the three reactions, oxygen evolution, oxidation of nitric oxide to nitrogen dioxide and reduction of nitric oxide. The electrodes are more active in the nitric oxide containing atmosphere

Table 1 Maximum cathodic current densities at a potential of −0.8 V versus air measured on the cone-shaped electrodes in either air or nitric oxide at three different temperatures

s	0.01		0.05		0.10		0.15		0.20		0.25	
T	Air	NO	Air	NO	Air	NO	Air	NO	Air	NO	Air	NO
200 °C	0.10	0.05	0.02	0.02	–	0.03	–	0.05	–	0.04	–	0.06
300 °C	2.5	1.8	6.0	1.0	3.0	0.5	2.0	0.3	1.0	0.4	0.6	1.1
400 °C	47	30	30	10	30	5.5	14	4.1	10	3.4	10	3.0

The current densities are given in mA cm^{-2} s is s in $(Pr_{0.6}Sr_{0.4})_{1-s}Fe_{0.8}Co_{0.2}O_{3-\delta}$. The current densities are seen to decrease with increasing *s*

Table 2 The maximum anodic current densities in the nitric oxide containing atmosphere recorded at 400 °C

s	0.0100	0.0500	0.1000	0.1500	0.2000	0.2500
I_{maxr}	11.5000	0.8000	3.0000	4.0000	4.5000	2.7000

The current density is highest for the $(Pr_{0.6}Sr_{0.4})_{0.99}Fe_{0.8}Co_{0.2}O_{3-\delta}$ perovskite

than in air at 200 °C, whereas the electrodes becomes more active in air at higher temperatures of 300 and 400 °C, that is the activation energy towards the reduction of oxygen is higher than the activation energy towards the reduction of nitric oxide. This shows that the apparent selectivity, towards nitric oxide reduction, is highest at the lowest temperatures. The magnitude of the current densities is, however, very low at the lowest temperatures.

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