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Activation/Deactivation Phenomena in the Electrochemical Reduction of Nitric oxide and Oxygen on LSM perovskites

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The effect of anodic pretreatment on $\text{LaMnO}_{3+\delta}$, $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_{3+\delta}$ and $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ point electrodes were investigated using cyclic voltammetry in the temperature range 200 to 400 °C in either 10% oxygen in argon or 1% nitric oxide in argon. The electrodes, in most cases, were deactivated in oxygen-containing gas and activated in nitric oxide-containing gas after anodic polarization. This was thought to be due to potential-induced SrO segregation to the surface of the electrodes and annihilation of oxygen vacancies. This work shows that the effect in some cases is significant and must be considered when evaluating the electrodes. In addition, the activity of the electrodes increases with increasing strontium content with respect to the reduction of both oxygen and nitric oxide. The electrodes were all more active with respect to the reduction of nitric oxide than with respect to the reduction of oxygen in the investigated temperature range.

Keywords: LSM; NO; O₂; Activation; Deactivation

1. INTRODUCTION

Pollutants emitted from the combustion of fuels in diesel-fired engines is of major concern. Among the unwanted pollutants are carbon monoxide, hydrocarbons, particulate matter and nitrogen oxides [1]. The removal of nitrogen oxides has proven difficult as the exhaust from diesel-fired engines contains excess oxygen [2]. However, several techniques have been developed to remove nitrogen oxides from exhaust containing excess oxygen, including the selective catalytic reduction (SCR) of nitrogen oxides with a reducing agent, typically urea [3]. The main drawback of SCR technology is the need for a reducing agent, which must be stored on board the vehicle. There is also the possibility of reducing agent slip.

An alternative to SCR technology is the removal of nitrogen oxides using an electrochemical reactor, as suggested by Pancharatnam et al. [4]. In that case the current is used directly to reduce the nitrogen oxides, instead of the need of a reducing agent, avoiding the aforementioned problems with storage and slip. Several issues need to be solved before the electrochemical approach can be implemented. The main obstacle is low current efficiency due to simultaneous reduction of oxygen at the cathode and a low activity at the diesel exhaust temperature [5].

Perovskites have been suggested as cathodes for the electrochemical reduction nitrogen oxides under net oxidizing conditions as they show the ability to reduce nitric oxide to nitrogen [6]. Perovskites are well known as oxygen reduction cathodes in solid oxide fuel cell technology because they exhibit chemical stability and good electronic conductivity [7]. The 'classical' solid oxide fuel cell cathode is $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_{3+\delta}$ (LSM15), but other types of perovskite-based cathodes have also been investigated [8]. Reproducibility is a major issue when studying solid oxide based electrodes. Several reasons for this have been put forward. Two of them are the differences in the microstructure of the electrodes, or the difference in the content of impurities in the electrodes [9, 10]. In this study, another reason for non-reproducible results is suggested as the effect of electrochemical pretreatment of the electrodes.

Here, LSMx ($\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3+\delta}$, $x = 0.00, 0.15$ and 0.50 , where δ is oxygen non-stoichiometry) electrodes are studied using cone-shaped electrodes and cyclic voltammetry. The LSMx electrodes are studied in either oxygen- or nitric oxide-containing gases. The electrodes are chosen such that they are strontium-free and have a large redox activity (LSM00), they contain strontium and are redox active (LSM15), or they contain strontium but with no (or at least a very low) redox activity (LSM50) [11]. The redox activity is the amount of transition metal that changes oxidation state when a difference in oxygen partial pressure is applied. The voltammograms are recorded either without pretreatment or with anodic pretreatment at 0.4 V vs. air for 16 h.

Some studies of the activation phenomena of LSM electrodes in air have already been undertaken [12, 13], but here, we report for the first time the potential-induced activation/deactivation phenomena as a function of the composition of the LSM and, in addition, in a nitric oxide-containing atmosphere.

2. EXPERIMENTAL

Synthesis of the LSM00, LSM15 and LSM50 powders was achieved using the glycine-nitrate process [14]. Briefly, aqueous solutions of the metal nitrates were mixed in the desired stoichiometric ratio in a beaker. Glycine was then added. The solutions were heated on a hot plate until ignition. Finally, the powders were calcined in a box furnace in air at 1100 °C for 12 h. The phase purity of the synthesized compounds was evaluated using either a STOE Theta-Theta diffractometer, equipped with Cu K_α radiation or a Bruker D8 diffractometer also with Cu K_α radiation. The powders were then pressed into cylinders in an appropriate die. The cylinders were sintered in a box furnace in air at 1250 °C for 12 h. A small disk was cut for use in the XRD. The cone-shaped electrodes were fabricated from the cylinders using diamond tools. The dimensions of the cone-shaped electrodes were a base of

7.5 mm and an angle of 45°. For the electrochemical measurements, a setup with separate atmospheres for the working and counter/reference electrodes was used. The setup has been described in more detail elsewhere [15]. A schematic drawing of the setup is shown in Fig. 1. The setup is a pseudo-three-electrode setup since the area of the counter/reference electrode is much larger than the area of the working electrode.

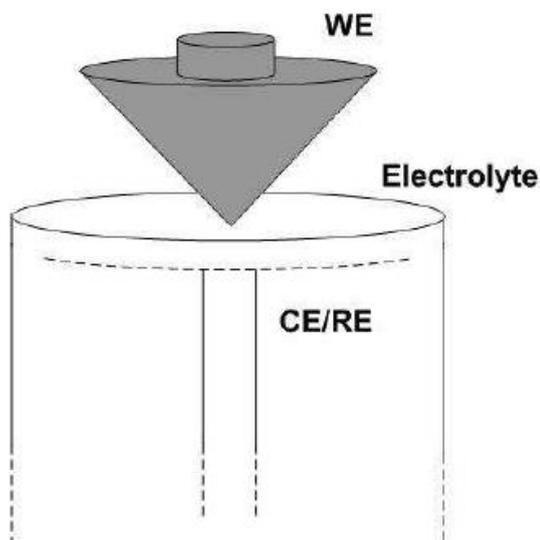


Figure 1. A schematic drawing of the cone electrode setup used in this study. The cone is pressed towards the one-end closed zirconia tube with small weight. The setup is a two-atmosphere setup with separate atmospheres for the working (cone) electrode and the reference/counter electrodes. The setup is a pseudo-three-electrode setup.

A platinum reference/counter electrode was used. The platinum was added as a paste (Degussa) and sintered at 1050 °C before use. The electrochemical measurements were done at 200, 300 and 400 °C. At each temperature the electrodes were equilibrated at 0.4 V vs. air for either 0 h or 16 h before recording the voltammograms. The voltammograms were recorded in the potential range 0.4 V vs. air to -0.8 V vs. air, starting at 0.4 V vs. air. The measurements were done in either 10% oxygen in argon or 1% nitric oxide in argon. A flow rate of 20 mL/min was used throughout. Electrochemical impedance spectroscopy (EIS) measurements were recorded at OCV in the oxygen-containing atmosphere at 500 °C to estimate the contact area of the point electrodes using Newman's formula [16]. EIS was initiated at 300 kHz and run down to 3 mHz with 6 points/decade and an amplitude of 36 mV rms. The electrodes were equilibrated for 2 h at OCV before recording the EIS data. For the electrochemical measurements, a Gamry Femtostat potentiostat was used.

3. RESULTS

The XRD results will be published elsewhere [17]. LSM00, LSM15 and LSM50 are shown to be single phase materials.

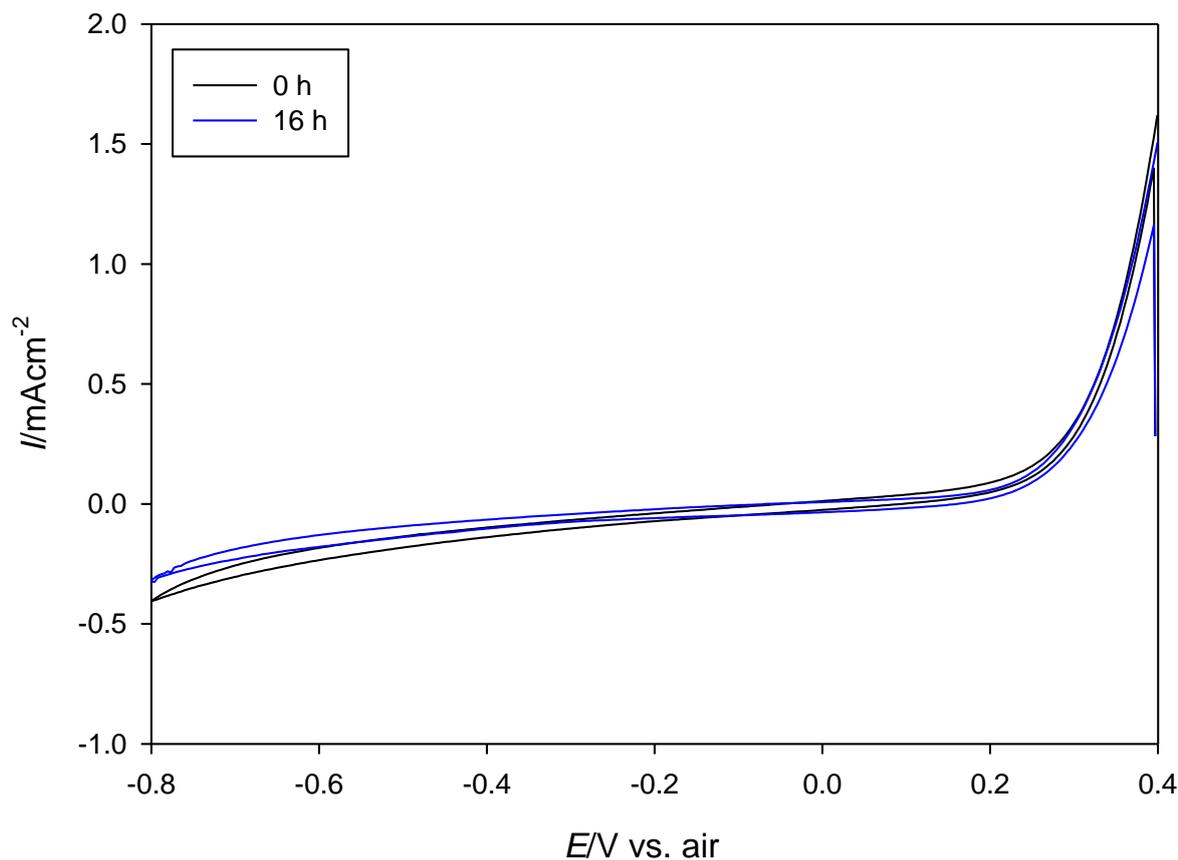
LSM00 @ 400 in O₂

Figure 2. Voltammograms recorded for LSM00 in 10% oxygen in argon at 400 °C with a sweep rate of 10 mV/s. The solid curve was recorded without anodic pretreatment, whereas the dotted curve was pretreated at a potential of 0.4 V vs. air for 16 h. The magnitude of the current densities is lowest for the LSM00 electrode treated at 0.4 vs. air before recording the voltammogram.

Voltammograms recorded under different conditions and on different materials are shown in Fig 2 to 7. The shape of the voltammograms is much similar on all the electrode materials and in both the oxygen- and nitric oxide-containing atmospheres, as they show curvature in both the anodic and cathodic potential regime. Manganate-based perovskites exhibit capacitive hysteresis in both the anodic and cathodic potential region. In general, the magnitude of the current densities is higher in the anodic potential regime than in the cathodic current regime in both the oxygen- and nitric oxide-containing atmospheres. The voltammograms recorded from LSM00 in the oxygen-containing atmosphere at 400 °C pretreated at 0.4 V vs. air for 16 h is shown in Fig. 2 together with the voltammogram recorded without prepolarization. The electrode is deactivated in the cathodic potential regime when the electrode has been prepolarized at 0.4 V vs. air. The same trend is observed at 200 and 300 °C. In the nitric oxide-containing atmosphere, the opposite trend is observed; that is, the electrode is activated in the cathodic potential regime upon pretreatment at anodic potential, see Fig. 3.

Also, this trend is observed at all the temperatures investigated in this study. The result of polarizing the LSM15 electrodes at 0.4 V vs. air in the oxygen-containing atmosphere before recording the voltammograms can be found in Fig. 4. The activity in the cathodic potential regime when measuring in the oxygen-containing atmosphere is increased after treatment at 0.4 V vs. air compared to the activity for the electrode that was not treated at 0.4 V vs. air.

LSM00 in NO @ 400 °C

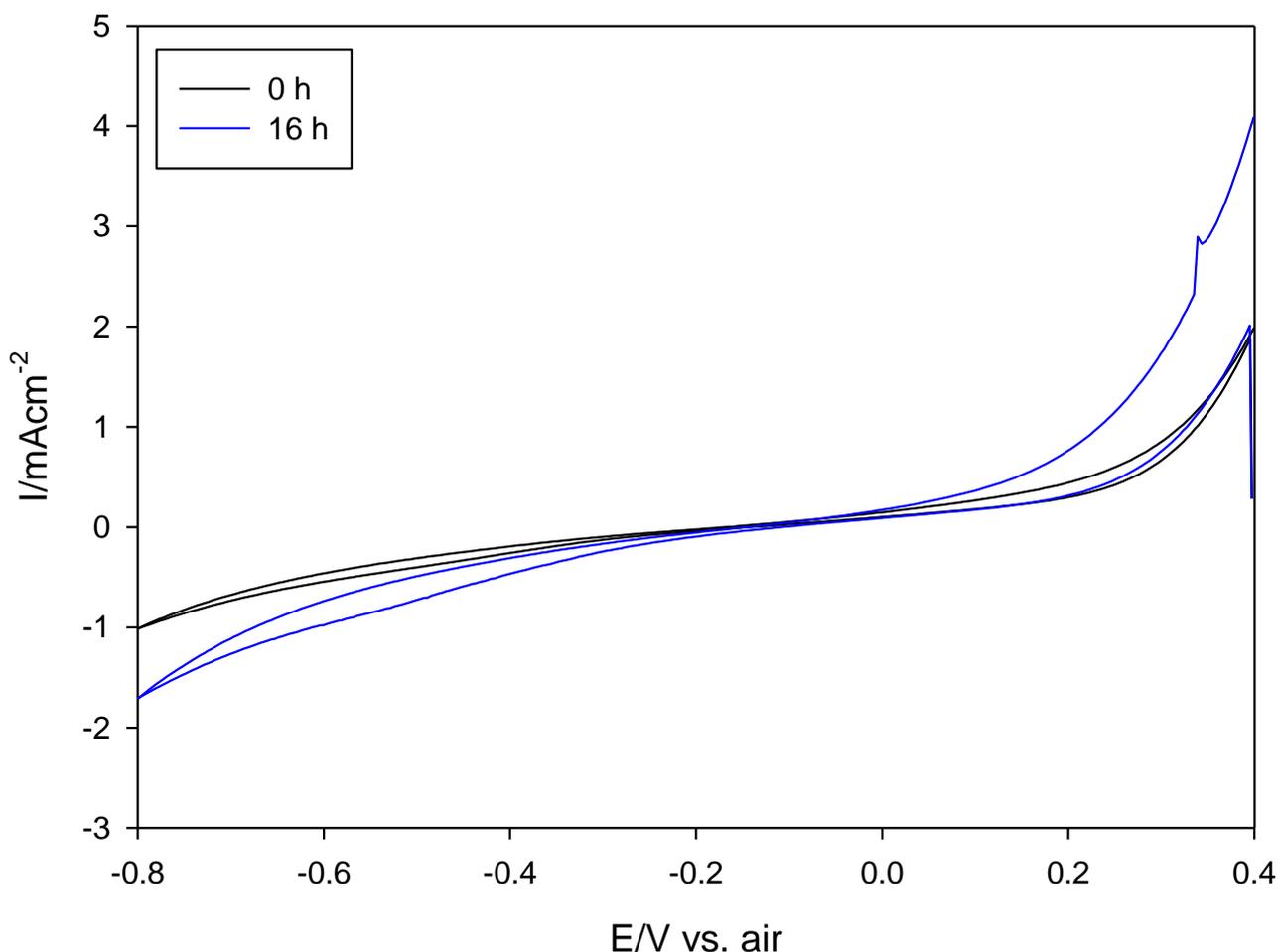


Figure 3. Voltammograms recorded for LSM00 in 1% nitric oxide in argon at 400 °C with a sweep rate of 10 mV/s. The solid curve was recorded without anodic pretreatment, whereas the dotted curve was pretreated at a potential of 0.4 V vs. air for 16 h. The magnitude of the current densities is highest for the LSM00 electrode treated at 0.4 V vs. air before recording the voltammogram.

In the nitric oxide-containing atmosphere the opposite trend is observed (see Fig. 5). However, there is an exception for LSM15 at 200 °C in the oxygen-containing atmosphere (not shown), where

the opposite trend is observed; that is, the electrode is more active after pretreatment at 0.4 V vs. air for 16 h in the oxygen-containing atmosphere. For the LSM50 electrode, voltammograms are shown in Figs. 6 and 7. In the oxygen-containing atmosphere none or only a very small effect is observed upon polarizing the LSM50 electrode before recording the voltammogram (Fig. 6). In contrast, a large effect is observed in the nitric oxide-containing atmosphere upon pre-treating the LSM50 electrode at 0.4 V vs. air for 16 h because the magnitude of the current densities is much larger after anodic pretreatment of the LSM50 electrode (see Fig. 7). The open circuit voltage (OCV) in the nitric oxide-containing atmosphere is given in Table 1 for the three compounds. The OCV is seen to increase with increasing strontium content.

LSM15 in O₂ @ 400 °C

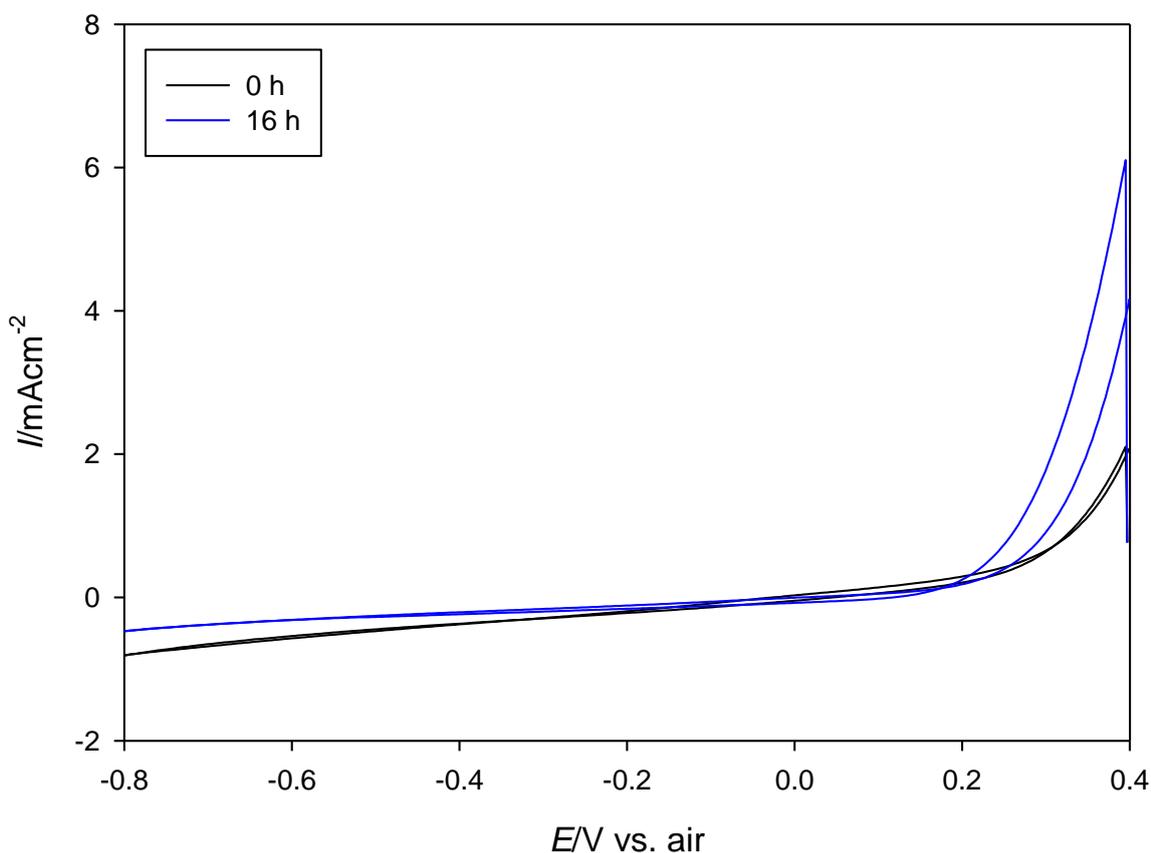


Figure 4. Voltammograms recorded for LSM15 in 10% oxygen in argon at 400 °C with a sweep rate of 10 mV/s. The solid curve was recorded without anodic pretreatment, whereas the dotted curve was pretreated at a potential of 0.4 V vs. air for 16 h. The magnitude of the current densities is lowest for the LSM00 electrode treated at 0.4 vs. air before recording the voltammogram.

LSM15 in NO @ 400 °C

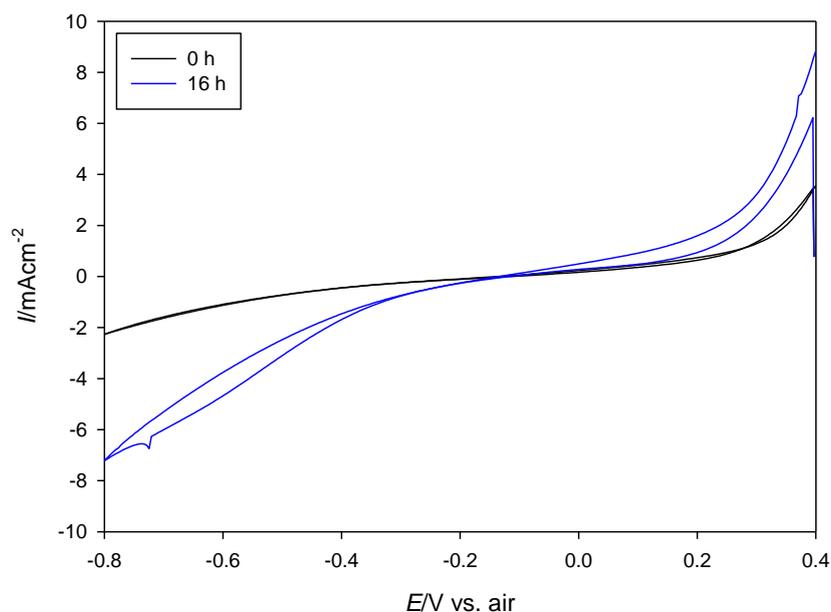


Figure 5. Voltammograms recorded for LSM15 in 1% nitric oxide in argon at 400 °C with a sweep rate of 10 mV/s. The solid curve was recorded without anodic pretreatment, whereas the dotted curve was pretreated at a potential of 0.4 V vs. air for 16 h. The magnitude of the current densities is highest for the LSM00 electrode treated at 0.4 V vs. air before recording the voltammogram.

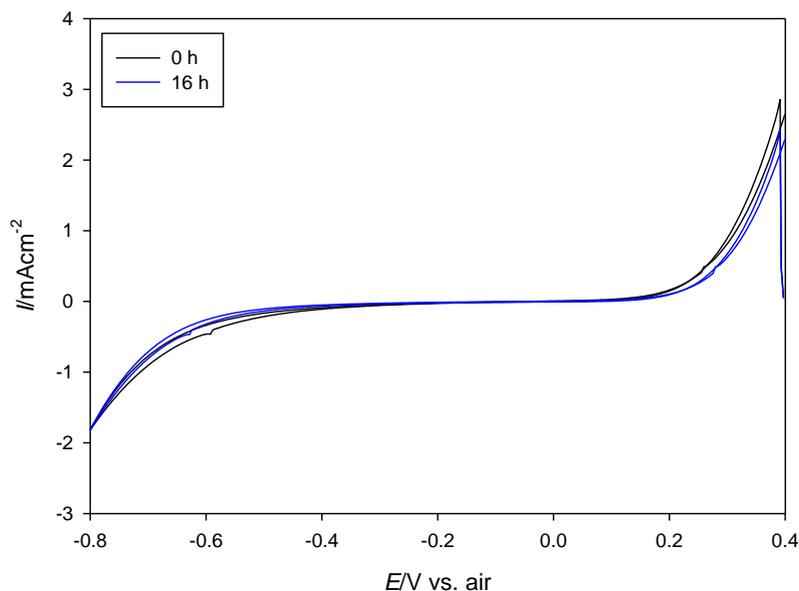
LSM50 in O₂ @ 400 °C

Figure 6. Voltammograms recorded for LSM50 in 10% oxygen in argon at 400 °C with a sweep rate of 10 mV/s. The solid curve was recorded without anodic pretreatment, whereas the dotted curve was pretreated at a potential of 0.4 V vs. air for 16 h. The magnitude of the current densities is lowest for the LSM00 electrode treated at 0.4 V vs. air before recording the voltammogram.

LSM50 in NO @ 400 °C

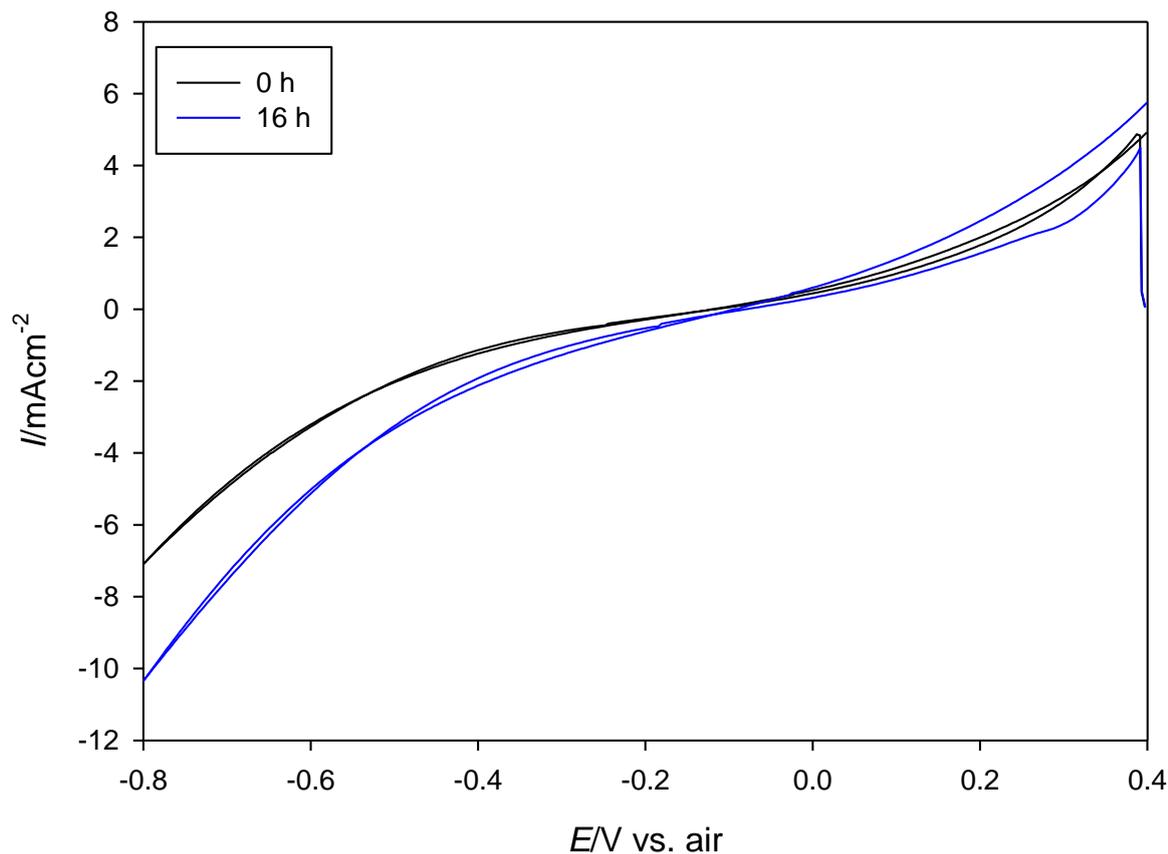


Figure 7. Voltammograms recorded for LSM50 in 1% nitric oxide in argon at 400 °C with a sweep rate of 10 mV/s. The solid curve was recorded without anodic pretreatment, whereas the dotted curve was pretreated at a potential of 0.4 V vs. air for 16 h. The magnitude of the current densities is highest for the LSM00 electrode treated at 0.4 V vs. air before recording the voltammogram.

Table 1. The OCV in the nitric oxide-containing atmosphere at 400 °C. The OCV is seen to decrease with increasing strontium content.

Composition	OCV
LSM00	-0.141 V
LSM15	-0.124 V
LSM50	-0.115 V

4. DISCUSSION

In general, the magnitude of the cathodic current densities is lower after anodic pretreatment of the manganate-based electrodes in the oxygen-containing atmosphere, even though the effect is very small for the LSM50 electrode. This can be related to the number of oxygen vacancies in the

manganates and the segregation of SrO to the electrode surface for LSM15 and LSM50. However, the oxygen stoichiometry of LSM00 and LSM15 changes when the oxygen partial pressure is changed at oxygen partial pressures of approximately 0.1 atm; this does not occur for LSM50. This difference can explain the behavior in the oxygen-containing atmosphere because anodic treatment of the electrodes causes annihilation of oxide ion vacancies in the LSM00 and LSM15 electrodes. An exception is found for LSM15 at 200 °C, where the effect is the opposite. The reason for this exception is not known. However, the kinetics must be very slow at 200 °C, and an adjustment of the oxygen stoichiometry will be very slow at these low temperatures, which might hide the actual effect of anodic pretreatment. The difference between the electrodes pretreated at 0.4 V for 16 h compared to the un-treated electrodes in the nitric oxide-containing atmospheres is the opposite of the effect observed in the oxygen-containing atmosphere. Since the effect is larger for LSM15 and LSM50 than for LSM00, this could indicate that the presence of strontium is important. As suggested in the literature, SrO might segregate to the surface of the electrode under anodic polarization [12]. It has been shown that the addition of small amounts of alkaline-earth oxides to LSM-based electrodes has a great effect on the ability of the electrode to reduce nitric oxide [19]. A suggestion could therefore be that nitrates are formed on the surface of the electrodes when the electrodes are polarized at 0.4 V vs. air for 16 h. The ability of alkaline-earth oxides to form nitrates is well known. BaO is used in NO_x storage and reduction catalysts [18]. It is speculated that the nitrates catalyze the reduction of nitric oxide to nitrogen [19]. Another general feature is that the magnitude of the cathodic current densities in the oxygen-containing atmosphere increases with increasing strontium content, but the effect is not very large. This could be due to an increasing number of oxygen vacancies and a higher electronic conductivity for manganates with higher strontium content. The results in the oxygen-containing atmosphere confirm to some extent earlier results for manganate-based perovskites [20]. The trend obtained from the manganate-based electrodes in the nitric oxide-containing atmosphere is the same as the trend obtained from the oxygen-containing atmosphere. The trend is the same whether or not the electrodes have been treated at anodic potentials before recording the voltammograms. The effect of anodic pretreatment on the manganate-based electrodes is largest for LSM15, indicating that two parameters control the enhancement of the activity of electrodes after anodic pretreatment, namely, the ability to segregate SrO and the redox activity. In general, a higher magnitude of the current densities in the nitric oxide-containing atmosphere is observed. The apparent selectivity is found to be highest for LSM50, the manganate-based perovskite, in contrast to earlier results that showed the apparent selectivity to be highest for the LSM15 manganate-based perovskite. The reason for this is not clear. However, in the literature, a ceria-based electrolyte was used instead of the zirconia-based electrolyte used in this study. The nitric oxide might adsorb differently on zirconia and ceria [21]. Additionally, as this work clearly shows, the effect of pretreatment is important for the performance of the electrodes. The reason LSM50 is the most active towards reduction of nitric oxide could be due to the high amount of strontium in this compound. The OCV in the nitric oxide-containing atmosphere is much lower than the calculated potential for the reduction of nitric oxide to nitrogen because the OCV is a mixed potential determined by three reactions, namely, the reduction of nitric oxide to nitrogen, the oxidation of nitric oxide to nitrogen dioxide and the evolution of oxygen. The dependence of OCV with composition also illustrates this. The better the cathode is at reducing nitric oxide, the higher the

OCV; the reduction of nitric oxide to nitrogen is initiated at higher potentials on the most active compounds.

5. CONCLUSION

The activity of LSM-based perovskites towards the reduction of oxygen and nitric oxide increases with increasing strontium content. This was thought to be due to an increasing number of oxide vacancies and higher electronic conductivity for the high strontium-substituted manganates. LSM-based perovskites are more active towards nitric oxide reduction than towards oxygen reduction in the temperature range 200 to 400 °C. Manganate-based perovskite electrodes can be either deactivated or activated when treated at anodic potentials. The LSM perovskites are activated in nitric oxide-containing atmospheres and deactivated in oxygen-containing atmospheres due to the annihilation of oxide ion vacancies and the segregation of SrO in the case of oxygen and is also due to the enhanced formation of nitrates by the segregation of SrO in the case of nitric oxide.

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