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Activation/Deactivation Phenomena's in the Electrochemical Reduction of O₂ and NO on La_{1-x}Sr_xFeO_{3-δ}

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ABSTRACT

Three ferrite based perovskites were investigated as cathodes for the electrochemical reduction of oxygen and nitric oxide, using cone-shaped electrodes and cyclic voltammetry. The ferrites investigated were LaFeO₃, La_{0.85}Sr_{0.15}FeO_{3-δ} and La_{0.5}Sr_{0.5}FeO_{3-δ}. Especially the effect of anodic pre-treatment of the electrodes was investigated. It was shown that the ferrite based electrodes are better at reducing nitric oxide than oxygen in the temperature range 200 to 400°C. The ability of the ferrites to reduce oxygen depends mainly on the amount of Fe(III) and oxide anion vacancies, leading to the highest activity towards the reduction of oxygen for the intermediate compound La_{0.85}Sr_{0.15}FeO_{3-δ} in the investigated temperature range. All the electrodes were either activated or de-activated when polarized at 0.4 vs. air, before recording the voltammograms, depending on temperature and gas atmosphere. This was attributed to annihilation of oxide ion vacancies, strontium segregation to the surface of the electrodes and perhaps formation of Fe(IV). The effect of water vapor was also studied. It had a slightly deactivating effect on the activity in the nitric oxide containing atmosphere, the effect being highest at the lowest temperatures.

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Keywords : Nitric Oxide, Oxygen, LSF

1. Introduction

Pollution from vehicles is a still increasing problem mainly in dense populated areas. Diesel driven vehicles emit soot, hydrocarbons, carbon monoxide and nitrogen oxides.¹ In order to remove the nitrogen oxides, it is necessary to use a suitable catalyst and add a reducing agent in form of typically urea or ammonia, due to the excess oxygen in the exhaust gas.² This is known as the selective catalytic reduction of nitrogen oxides (SCR). An alternative approach is to use an electrochemical reactor for the deNO_x process, as suggested by Pancharatnam et al.³ In such a reactor the nitrogen oxides are reduced to nitrogen and oxide anions at the cathode when the reactor is polarized. The oxide anions is then transported through the electrolyte to the anode, where either there is oxygen evolution, or alternatively the oxide anions react with the soot, hydrocarbons or carbon monoxide. The main obstacles are the low activity at the relatively low temperature of the Diesel exhaust and a low selectivity leading to high power consumption, due to simultaneously reduction of the oxygen at the cathode.⁴

Several studies have addressed this need for a highly selective cathode.⁵⁻⁷ Among the different families of materials studied are noble metals, simple oxides, spinels and perovskites.⁴ One type of perovskite material is La_{1-x}Sr_xFeO_{3-δ} (LSFxx). LSF has been studied using point electrodes for the reduction of nitrous oxide,⁸ nitric oxide⁹ and nitrogen dioxide.¹⁰ The ferrites have shown the ability to reduce all three types of nitrogen oxides electrochemically. Ferrites may show instability in the presence of water vapor.¹¹

In this text the deactivation/activation processes in the electrochemical reduction of oxygen and nitric oxide, with and without water vapor, when treating the electrodes at anodic potentials before characterizing them electrochemically, is described. The deactivation/activation processes is studied using cone-shaped electrodes and cyclic voltammetry. There are several advantages of using cone-

shaped electrodes. First of all the electrode and the electrolyte are fabricated separately, thereby avoiding reaction during processing at high temperature. Second, the contact point is in principle simple, and the contact area of the cone-shaped electrode can be determined by electrochemical impedance spectroscopy and Newman's formula.¹² A drawback is that it is not possible to do gas analysis, due to the small size of the contact point between the cone-shaped electrode and the electrolyte.

The activation/deactivation of La_{1-x}Sr_xMnO_{3+δ} (LSM) based SOFC cathodes have been extensively studied in the literature.¹³⁻²⁰ Several mechanisms have been suggested, among them the segregation of strontium to the surface of the electrode during anodic pretreatment of the cathode, leading to deactivation of the cathode, has been proposed.¹⁶ No studies have been given in the open literature on these phenomena's on LSF based perovskites so far.

The electronic properties and defect chemistry of LSF based perovskites has also been investigated extensively in the literature. LSF perovskites are known to be mixed electronic and ionic conductors.²¹⁻³³ Both the electronic and ionic conductivity finds its maximum for the LSF50 perovskite.³³ The electronic conductivity is p-type.

2. Experimental

Synthesis of the ferrites was done using the glycine-nitrate process.³⁴ The procedure is as follows: First aqueous solutions of metal-nitrates were mixed in a beaker in the appropriate ratio. Glycine was then added. The solution was placed on a hot plate and heated until ignition. After this the resulting powders were transferred to an alumina crucible and placed in a chamber furnace. The powders were calcined for 12 h at 1100°C in air. The metal-nitrates used for the synthesis of the LSF perovskites were:

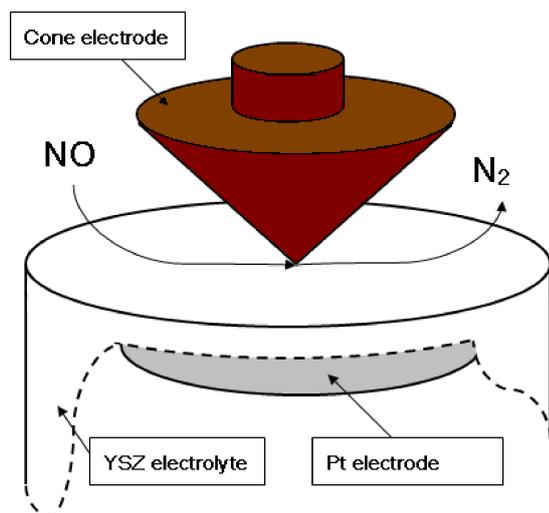


Figure 1. A schematic drawing of the experimental setup used in this study. The cone-shaped electrode (the working electrode) is pressed towards an yttria stabilized zirconia one-end closed tube, with approximately 60 g of weight. The setup is a two chamber setup. The inner of the tube is flushed with air, and contains a platinum reference/counter electrode. The working electrode is exposed to either 1% nitric oxide in argon or 10% oxygen in argon. Electrical connection to the working electrodes is done using a gold wire. The temperature is measured by a thermocouple in contact with the electrolyte.

$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar, 99.9%), $\text{Sr}(\text{NO}_3)_2$ (Alfa Aesar, 99%) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Alfa Aesar, 98%).

The phase purity of the ferrites was checked using powder XRD on a Stoe theta-theta diffractometer.

After calcination the 7–8 g of the powders were pressed into a cylinder in a suitable die. The cylinders were sintered at $1250^\circ\text{C}/12\text{ h}$ in a box furnace in air. Finally the cylinders were machined into cones with a base of 7.5 mm by the use diamond tools. The electrochemical measurements were done in a setup as shown in Fig. 1. The setup is a two-atmosphere where the reference/counter electrode is exposed to air, and the working electrode (the cone) is exposed to either oxygen or nitric oxide containing atmospheres. The setup is a pseudo three electrode setup as the area of the counter/reference electrodes is many times larger than the contact area of the cone-shaped electrode. The reference/counter electrode is made by painting with Pt-paste. As an electrolyte a one-end closed yttria stabilized zirconia tube was used. The part of the zirconia tube in contact with the working electrodes was polished down to $1\ \mu\text{m}$. The electrochemical measurements were done using a Gamry femtostat potentiostat. The cones were kept at $0.4\ \text{V vs. air}$ for 0, 2, 4, 8 and 16 h before recording the voltammograms. As a sweep rate $1\ \text{mV/s}$ was used throughout. The voltammograms were recorded at 200, 300 and 400°C in either 1% nitric oxide in argon or 10% oxygen in argon. For LSF15 3% of water vapor was also added to the nitric oxide containing atmosphere. Potential limits were $0.4\ \text{V vs. air}$ to $-0.8\ \text{V vs. air}$. The electrochemical impedance was recorded at 400°C . The impedance was recorded from 300 kHz to 3 mHz with 6 points pr. decade and a rms amplitude of 36 mV at open circuit voltage (OCV). From the impedance data the series resistance was found, in order to determine the contact area of the working electrode from Newman's formula.

3. Results

The results of the X-ray powder diffraction has been published in a previous work.¹⁰ All the ferrites were shown to be single phased

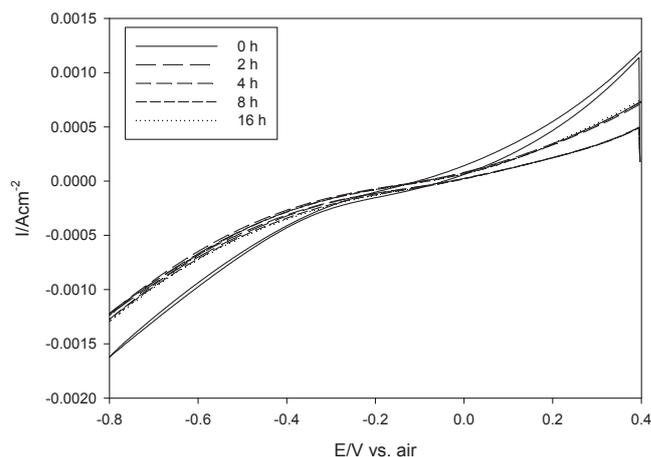


Figure 2. Voltammograms recorded on LSF00 in a nitric oxide containing atmosphere at 300°C . The voltammograms are recorded after 0, 2, 4, 8 and 16 h of pre-polarization at $0.4\ \text{V vs. air}$. It is observed that the electrode de-activates after polarization at $0.4\ \text{V vs. air}$ for 2 h, where after the electrode is stable. The voltammograms shows curvature in both the anodic and cathodic potential regimes.

Table 1. Maximum cathodic current densities at 200, 300 and 400°C in either 1% nitric oxide in argon or 10% oxygen in argon on LSF00, LSF15 and LSF50. The current densities are seen to be larger in the nitric oxide containing atmosphere, than in the oxygen containing atmosphere. The current densities are largest at the highest temperature. When water vapor is added to the nitric oxide containing atmosphere, the current densities decreases slightly. Units is μAcm^{-2} .

Compound	LSF00		LSF15			LSF50		
	T/Gas	O ₂	NO	O ₂	NO	NO/H ₂ O	O ₂	NO
200°C		0.02	0.13	0.03	0.30	0.20	0.02	0.17
300°C		0.47	1.60	5.00	6.00	4.00	0.26	1.50
400°C		1.70	11.4	10.0	22.0	20.0	1.50	2.90

and belonged to the orthorhombic crystal system. Representative voltammograms are shown in Figs. 2 to 8. Maximum cathodic current densities are given in Table 1. In general the voltammograms have the same shape on all the ferrites and in both the nitric oxide containing atmosphere and in the oxygen containing atmosphere. That is the voltammograms shows curvature in both the anodic and cathodic current directions. Also in general the current densities are highest on the intermediate compound LSF15 in the oxygen containing atmospheres and at all temperatures, in fair agreement with our earlier publications.^{9,35}

In Fig. 2 the voltammograms recorded at 300°C in the nitric oxide containing atmosphere is shown. It is seen that the current densities finds a minimum already after only two hours of polarization at $0.4\ \text{V vs. air}$. From 4 h and to 16 h only a minimal change is observed in the voltammograms. In contrast to this the current densities are seen to decrease with prolonged polarization at $0.4\ \text{V vs. air}$ in the oxygen containing atmosphere, see Fig. 3. The current densities are higher in the nitric oxide containing atmosphere than in the oxygen containing atmosphere on the un-doped ferrite. At 200°C the current densities in the nitric oxide containing atmosphere continues to decrease even after 16 h of polarization at $0.4\ \text{V vs. air}$. In the oxygen containing atmosphere the opposite is observed. The current densities is a factor of around 10 higher in the nitric oxide containing atmosphere, than in the oxygen containing

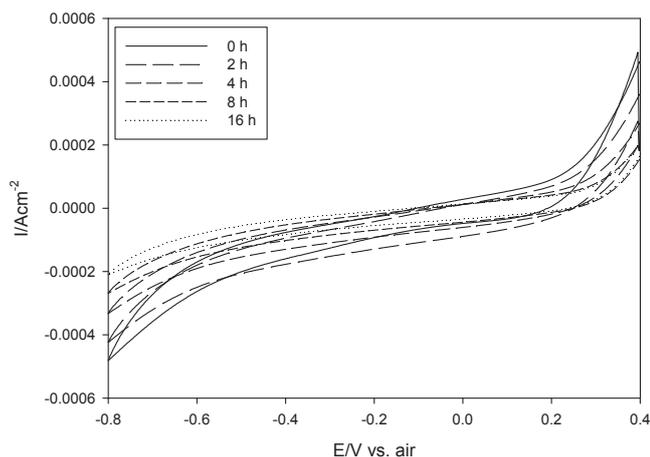


Figure 3. The voltammograms recorded at 300°C on the LSF00 ferrite in an oxygen containing atmosphere, is plotted in the figure. The voltammograms is recorded after pre-polarization at 0.4 V vs. air for 0, 2, 4, 8 and 16 h. It is seen that the electrodes continue to deactivate even after 16 h of polarization at 0.4 V vs. air. All the voltammograms show curvature in both the anodic and cathodic potential regimes.

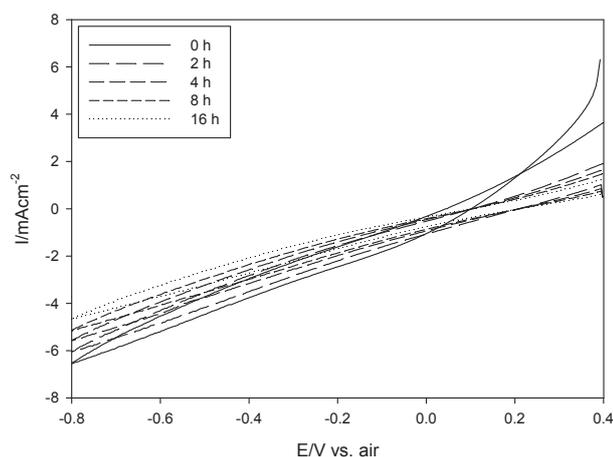


Figure 4. Voltammograms recorded on LSF15 in a nitric oxide containing atmosphere at 300°C. The voltammograms is recorded after 0, 2, 4, 8 and 16 h pre-polarization at 0.4 V vs. air. All the voltammograms shows curvature in both the anodic and cathodic potential regimes. It is seen that the LSF15 electrode deactivates steadily after even 16 h of pre-polarization at 0.4 V vs. air.

atmosphere. At 400°C the same is seen in the nitric oxide containing atmosphere as at 300°C that a maximum current density is achieved after 2 h of polarization. In the oxygen containing atmosphere no effect of pre-polarization is observed on the LSF00 ferrite at 400°C.

For the intermediate ferrite, LSF15, voltammograms recorded at 300°C are plotted in Figs. 4, 5 and 6. In Fig. 4 it is seen that the magnitude of the current decreases in the nitric oxide containing atmosphere even after prolonged polarization at 0.4 V vs. air. The same is observed in the atmosphere where water vapor is present besides nitric oxide in the gas atmosphere. In the oxygen containing atmosphere a slight activation is observed at 300°C, see Fig. 6. A large hysteresis is observed. The current densities are higher on the LSF15 ferrite than for the LSF00 ferrite in both atmospheres. At 200°C a small activation is observed in the nitric oxide containing atmosphere after short time polarization at 0.4 V vs. air. After this a

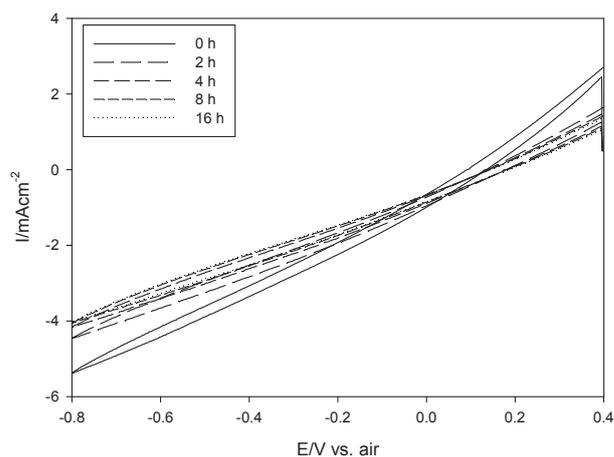


Figure 5. The behavior of the LSF15 in nitric oxide with water vapor is similar to the behavior in the nitric oxide containing atmosphere without water, that is the electrode continues to deactivate after even long time of anodic polarization. The currents are slightly lower in the atmosphere with water vapor than without water vapor.

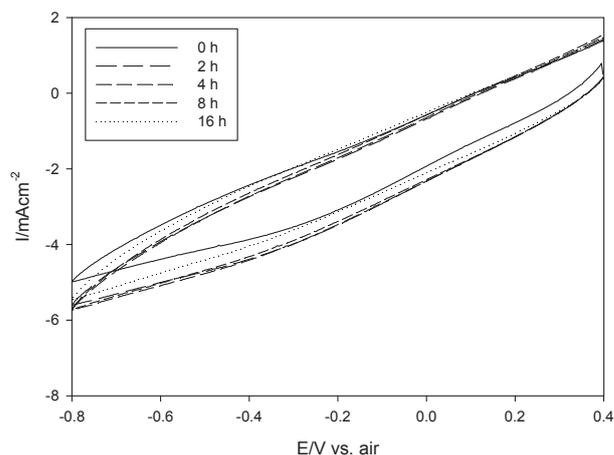


Figure 6. The recorded voltammograms on a LSF15 electrode in an oxygen containing atmosphere at 300°C are shown in the figure. All the voltammograms shows curvature in both the anodic and cathodic potential regimes. The voltammograms has been recorded after pre-polarization at 0.4 V vs. air for 0, 2, 4, 8 and 16 h. It is seen that the LSF15 based electrode continues to deactivate even after 16 h of pre-polarization at 0.4 V vs. air.

small decrease is observed. With water vapor almost no change is observed after pre-polarization. The currents are slightly lower when water vapor is present. As for LSF00 the current densities increase in the oxygen containing atmosphere at 200°C, after pre-polarization. At 400°C a small change is observed in the cathodic regime after pre-polarization in the nitric oxide containing atmosphere both with and without water vapor. In the oxygen containing atmosphere a small activation is observed after pre-polarization at 0.4 V vs. air.

For the strontium rich ferrite, LSF50, at 300°C, the same trend as for LSF00 and LSF15 is repeated, that is the current densities are stable after 2 h of polarization in the nitric oxide containing atmosphere, whereas the current densities continue to decrease in the oxygen containing atmosphere even after 16 h of polarization at 0.4 V vs. air, see Fig. 7. The current densities are smaller than for the LSF15 ferrite in both atmospheres. At 200°C the same is observed as for LSF15, with the exception that the LSF50 electrode

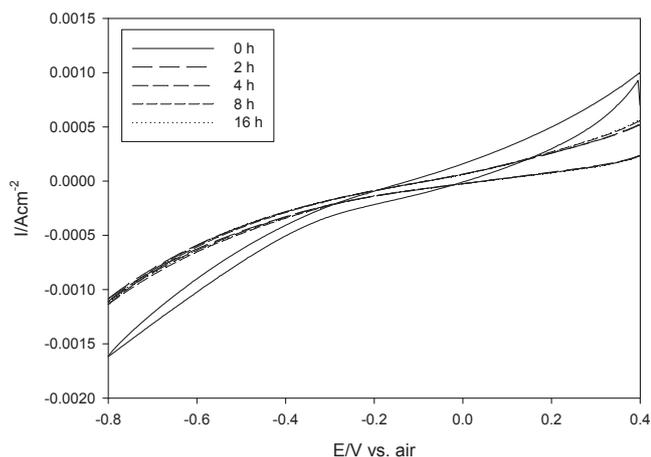


Figure 7. The behavior of a LSF50 based electrode in a nitric oxide containing atmosphere at 300°C. The electrode has been pre-polarized at 0.4 V vs. air for 0, 2, 4, 8 and 16 h before the voltammograms was recorded. Curvature is observed in both the anodic and cathodic potential regimes. The electrode deactivates after only 2 h of pre-polarization at 0.4 V vs. air, where after it is stable.

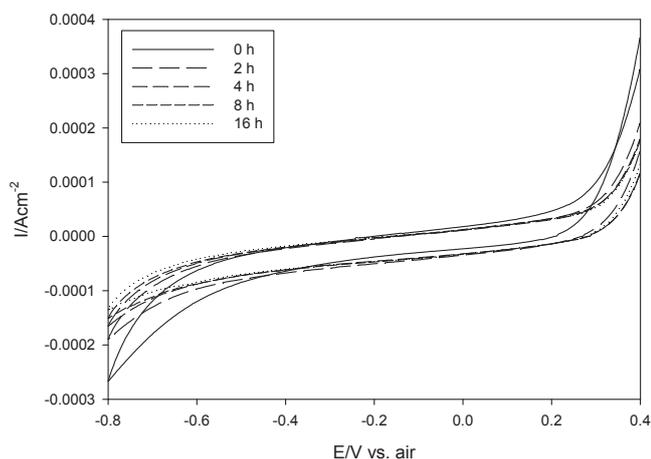


Figure 8. The figures shows voltammograms recorded on a LSF50 electrode in an oxygen containing atmosphere at 300°C. The electrode has been pre-treated at 0, 2, 4, 8 and 16 h at 0.4 V vs. air before the voltammograms were recorded. It is seen that the electrode continues to de-activate. The LSF50 electrode shows curvature in both the anodic and cathodic potential regimes.

still not is fully stabilized in the nitric oxide containing atmosphere after 16 h of polarization at 0.4 V vs. air. At 400°C a small activation is observed in the nitric oxide containing atmosphere after pre-polarization at 0.4 V vs. air. In the oxygen containing atmosphere no effect of pre-polarization is observed.

4. Discussion

The measurements in the oxygen and nitric oxides containing atmospheres are in fair agreement with our earlier published results.⁹ It is shown that the current densities are much smaller on the ferrites in the oxygen containing atmosphere than in the nitric oxide atmosphere at the lowest temperatures. The most active compound in the oxygen containing atmosphere at 400°C is the intermediate ferrite LSF15 as also seen in our earlier work at higher temperatures.³⁵ This indicates that two properties are needed in order to have a high activity towards oxygen reduction. These properties are

suggested to be the amount of Fe(III) and the amount of oxide ion vacancies.

The deactivation of the LSF00 electrode as a function of time in the nitric oxide containing atmosphere can be explained as follows. When the ferrite is polarized anodically Fe(III) may be oxidized to Fe(IV) leading to the creation of cation vacancies, and thereby following depletion of oxide anion vacancies in the surface of the electrode structure. At 200°C this process is very slow and the electrodes still deactivates after 16 h of anodically polarization. At higher temperatures the maximum activity of the ferrite is achieved already after 2 h of polarization, and only a weak change in the voltammograms is observed after this. It has been suggested for LSM that there is an upper limit to the amount of cation vacancies in the structure.³⁶ At higher temperature this excess of oxygen might be reached after less than 2 hours of polarization. In the oxygen containing atmosphere a slight activation is observed at 200°C as a function of time. The reason for this is not well understood. Perhaps again a small amount of Fe(IV) is formed and this may aid in the reduction of oxygen. It could also be due to a slight increase in the electronic conductivity, induced by the formation of Fe(IV). It should be noted that the currents in the oxygen containing atmosphere is much lower than in nitric oxide and therefore may be more sensitive to electrode changes. At 300°C a slight deactivation is observed, as it is the case in the nitric oxide containing atmosphere. The same reason could be due to this. At 400°C almost no effect of pre-polarization is observed in the oxygen containing atmosphere. At 400°C the electronic conductivity of LSF00 is higher than at 200°C and this could lead to the difference in behavior.³⁷

For LSF15 now we have strontium in the structure. The same is seen for LSF15 as for LSF00 at 200 and 300°C, and this indicates that the strontium is of less importance than for the manganites.¹⁶ At 400°C almost no change with pre-polarization is observed. The reason for why the LSF15 behave differently from the magnates could be because the Sr-segregation on LSF15 is slow compared to LSM based cathodes, which has cation vacancies, probably facilitating the diffusion of the cations. In the oxygen containing atmosphere the same trend is observed as for LSF00; that is activation at the lowest temperature investigated. This again suggests that the strontium content is of less importance than for the manganites. Again here the current densities are much lower in the oxygen containing atmosphere than in the nitric oxide containing atmosphere.

Water vapor has only a minor influence on the activity of the LSF15 ferrite in the nitric oxide containing atmosphere, suggesting that the ferrites can be used as an electrode in an exhaust gas containing water vapor. Also no significant degradation was observed in the presence of water vapor.

In the case of LSF50 we have the same behavior at 200 and 300°C in the nitric oxide containing atmosphere. However, at 400°C strontium segregation might be of importance for this the most strontium rich of the evaluated electrodes, leading to a little activation after prolonged pre-polarization at 400°C. This activation can be explained as follows; if strontium segregates to the surface of the electrode, there is a possible of formation of strontium-nitrates. Alkaline-earth compounds are known to enhance the activity of electrodes towards the reduction of nitric oxide significantly.^{6,7} The alkaline-nitrates act as a so called storage compound. However, the effect is still small compared to the effect on the manganites. The behavior in the oxygen containing atmosphere is almost the as for the two other ferrites studied, that is the activity of the ferrite is lowered upon pre-polarization.

As it can be seen, from this study, the behavior, of all the three ferrites, in the oxygen containing atmosphere, is almost the same. This again suggests that the strontium segregation is much smaller on the ferrites than on the manganites, which can easily be explained in the differences in the oxygen stoichiometry.

5. Conclusion

Oxygen and nitric oxide can be reduced on un-doped and strontium doped lanthanum ferrites. The ferrites were activated and de-activated in a complexes manner in the two atmospheres upon anodic pre-treatment. This was thought to be due to annihilation of oxygen vacancies and perhaps formation of Fe(IV). Water vapor has only a slight effect on the activity if the ferrites towards the reduction of nitric oxide.

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