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Electrochemical Reduction of Oxygen and Nitric Oxide at Low Temperature on $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ Cathodes

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Abstract: Six $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ ($x = 0, 0.05, 0.15, 0.25, 0.35, 0.50$) perovskites were synthesised and characterised by powder XRD and cyclic voltammetry on cone-shaped electrodes in either air or nitric oxide in argon at 200, 300 and 400°C. At 200°C the current densities in air was highest for the strontium free cobaltite, whereas the current densities was highest for $\text{La}_{0.95}\text{Sr}_{0.05}\text{CoO}_{3-\delta}$ in the nitric oxide containing atmosphere. This was also the compound with the highest $I_{\text{NO}}/I_{\text{O}_2}$ current ratio at 200°C. At higher temperatures a limiting cathodic current was observed for all of the cobaltite's, except $\text{La}_{0.50}\text{Sr}_{0.50}\text{CoO}_{3-\delta}$, in both air and the nitric oxide containing atmosphere. This was attributed to a rate limiting chemical step (i.e. dissociation of oxygen or nitric oxide) in the reaction sequence.

Introduction: The formation of nitric oxide in the combustion process in Diesel fired engines is well known [1]. This gives problems with pollution in the form of acid rain. NO_x is also harmful to human beings as it can lead to lung oedema [2]. Electrochemical reduction of nitric oxide is a potentially convenient technique to remove NO_x from Diesel exhaust gasses [3]. In an electrochemical cell, with an oxide anion-conducting electrolyte, the NO_x is reduced to nitrogen and oxide anions at the cathode. The oxide anions are removed from the cathode and are transported through the electrolyte to the anode where oxygen is formed. The main obstacle with this technique is the simultaneously reduction of

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oxygen at the cathode resulting in a high current consumption [4]. However, recently results have been presented in the literature that shows current efficiency in the vicinity of 20 % [5]. The electrode used to obtain the current efficiency of 20 % demand the use of an expensive noble metal in the form of platinum. The use of low cost electrodes is utmost importance, and the search for low cost electrodes is therefore ongoing [6-16]. Another problem is the activity at the low temperatures in the Diesel exhaust [17]. Perovskites with manganite and/or iron has been studied in the literature and some of them show high apparent selectivity's towards the reduction of nitric oxide in a net oxidising atmosphere [7-9]. However, the activity of these compounds might be too low. Among perovskites cobalt-based perovskites shows the highest activity towards the electrochemical reduction of oxygen [18]. Only a few studies of the electrochemical reduction of nitric oxide on cobalt-based perovskites have been reported in the literature [7, 19]. In this study the electrochemical reduction of oxygen and nitric oxide is studied in the temperature range 200 to 400°C on a series of cobalt-based perovskites, using cone-shaped electrodes and cyclic voltammetry.

Experimental: Synthesis of the perovskites was done using the glycine-nitrate process [20]. The synthesis was done as follows. First aqueous solutions of the metal-nitrates were mixed in the appropriate ratio in a beaker. Glycine was then added. The solutions were heated on a hot plate until ignition. The resulting fine powders were calcined in a box furnace in air at 1000°C/6 h. Powder XRD was performed to evaluate the formation of the perovskite phase. A Stoe theta-theta diffractometer equipped with $\text{Cu}_{k\alpha}$ radiation was used for this. After this the powders were pressed in an appropriate die and sintered at 1200°C/12 h in air. The cylinders were machined into cone-shaped electrodes using diamond tools. The cone-shaped electrodes were rinsed in EtOH in an ultra-sonic bath before use.

The electrochemical measurements were done in a two-atmosphere set-up, see Figure 1. As an electrolyte a one end closed YSZ (Yttria Stabilized Zirconia) tube (Vesuvius) was used. The closed end of the YSZ tube exposed to the cone-shaped electrode was polished with 1 μm diamond paste before use. As a reference gas air was used. As a counter/reference electrode platinum was used. The platinum was added as a paste (Engelhard) and sintered at 1000 °C/2 h in air. The set-up is a pseudo three electrode set-up as the area of the working electrode is many times smaller than the counter/reference

electrode. The electrochemical measurements were done at 200, 300 and 400°C in either air or 1% NO in Ar. Cyclic voltammetry was recorded between 0.4 to -1.0 V vs. air. The sweeps were initiated at OCV and run in the cathodic current direction first. Sweep rates used were 1 and 10 mV/s. To determine the contact area of the cone-shaped electrodes electrochemical impedance spectroscopy (EIS) was used together with Newman's formula [21]. The EIS was recorded at OCV from 1 MHz to 0.05 Hz with 6 points measured per decades. An amplitude of 36 mV was used throughout.

Results: The powder XRD reveals that the synthesised cobaltite's are of single phase. The cobaltite's were hexagonal for $x = 0, 0.05, 0.15$ and 0.25 . For $x = 0.35$ and 0.50 the cobaltite's were orthorhombic. After sintering the achieved density of the cylinders were better than 93 % of the theoretical value. Examples of voltammograms can be found in Figures 2 to 5. No significant difference was observed between the voltammograms recorded with sweep rates of 1 or 10 mV/s, so only the voltammograms recorded with a sweep rate of 1 mV/s is presented in the text. In Figure 2 voltammograms of the reduction of oxygen and nitric oxide at 200°C on LSCo50 is plotted. The LSCo50 cathode has almost equal activity in air and in the nitric oxide containing atmosphere. The maximum cathodic current is around -0.13 mAcm^{-2} in air and -0.09 mAcm^{-2} in the nitric oxide containing atmosphere. The reduction of oxygen and nitric oxide is initiated at almost the same potential, around 0 V vs. air. The voltammogram recorded in air is seen to be almost straight. In air a capacitive hysteresis is observed, in the cathodic potential region, on reversal of the scan direction. In the nitric oxide containing atmosphere some curvature (the curve bend downwards) is observed in the cathodic potential regime. Also here is a capacitive hysteresis observed upon reversal of the scan direction in the cathodic potential regime. In Figure 3 the reduction of nitric oxide and oxygen on LSCo50 at 300°C can be found. Again the maximum cathodic current density is larger in air than in the nitric containing atmosphere. The maximum current density in air is around -6 mAcm^{-2} whereas it is around -4 mAcm^{-2} in the nitric oxide containing atmosphere. The hysteresis observed in the Figure is capacitive in both atmospheres. In Figure 4 the voltammograms recorded on LSCo50 at 400°C in either air or the nitric oxide containing atmospheres are shown. The cathodic currents are almost identical in the two atmospheres. Again the electrodes exhibit capacitive hysteresis in the cathodic region. At higher temperatures (at 300 and 400°C) a rate limiting cathodic current is observed for all the cobaltite's,

except LSCo50, in both air and the nitric oxide containing atmosphere. This is illustrated in Figure 5 where the voltammograms recorded on LSCo15 in air and nitric oxide at a temperature of 300°C is plotted. It is seen that the maximum cathodic current densities is almost the same in air and the nitric oxide containing atmosphere. This is observed for all the cobaltites that exhibit the behaviour with a limiting current density, except for LSCo0. The behaviour of the cobaltites in the anodic potential region is almost the same for all the electrode materials. The maximum anodic current densities are much higher in the nitric oxide containing atmosphere than in air. In Figure 6 the maximum cathodic current densities in air at 200°C are plotted. The current densities in air are highest for the strontium free cobaltite, with a maximum cathodic current of 0.6 mAcm⁻². From LSCo5 to LSCo50 a small increase in the maximum cathodic current is observed at 200°C. The maximum current densities in the nitric oxide containing atmosphere at 200°C is plotted in Figure 7. The highest current densities in the nitric oxide containing atmosphere at 200°C is found for LSCo5. The current ratios (I_{NO}/I_{O_2}) at 200°C are given in Figure 8. LSCo5 is seen to have the highest current ratio at 200°C, as the current is almost a factor of five higher in the nitric oxide containing atmosphere than in air. The current ratio for LSCo15, 25, 35 and 50 are almost identical. The maximum cathodic current densities in air or the nitric oxide containing atmospheres at all three temperatures are given Table 1. The maximum current densities increase with increasing temperature.

Discussion: The rate of the reduction of oxygen at 200°C is highest on the strontium free cobaltite. However, the trend for the rest of the cobaltites is as observed at higher temperatures that are the activity towards the reduction of oxygen increases with increasing strontium content [22]. This can be attributed to increased amount of oxide ion vacancies and a higher electronic conductivity for the strontium rich cobaltites [23]. At 200°C the ionic conductivity of the cobaltites is very low, and the mobility of the oxide ion vacancies is very low [24]. However, an increased amount of oxide ion vacancies in the bulk of the electrode will lead to more oxide ion vacancies on the surface of the electrodes. Oxide ion vacancies on the surface are generally believed to be the catalytic active sites on perovskite based materials [25]. The electronic conductivity increases with increasing strontium content at 200°C [26], and an increased electronic conductivity might ease the reduction of oxygen. That the strontium free cobaltite is the best oxygen reduction cathode at the low temperatures used in

this study, is therefore a bit surprising. A possible explanation could be that strontium segregates to the surface of the electrode, blocking some of the active sites, for the strontium containing cobaltites. The reduction of nitric oxide is initiated at potentials much lower than the calculated potential for the reduction of nitric oxide [4]. This is due to competing reactions at the electrode. Besides the reduction of nitric oxide, also oxidation of nitric oxide to nitrogen dioxide and evolution of oxygen are possible reactions in the nitric oxide containing atmosphere. These two reactions inhibit the reduction of nitric oxide. The OCV in the nitric oxide containing atmosphere is therefore a mixed potential. The low OCV in the nitric oxide containing atmosphere has also been observed for other types of electrodes [4]. This means that we cannot benefit from the thermodynamic fact that nitric oxide is less stable than oxygen, as the reduction of nitric oxide first is initiated below the potential where the reduction oxygen is initiated. The reduction of nitric oxide will therefore always be in competition with the reduction of oxygen, in a gas mixture of nitric oxide and oxygen. The selectivity of a cathode for the reduction of nitric oxide in a gas mixture of nitric oxide and oxygen will therefore depend on the kinetics. The limiting cathodic current densities observed for LSCo0, 5, 15, 25 and 35 at 300 and 400°C could be due to a rate limiting chemical reaction step in the reaction sequence. This rate limiting step could be the dissociation of oxygen or nitric oxide on the surface of the electrodes or the diffusion of oxide anions through the bulk of the electrode. No limiting cathodic current were observed for LSCo50. This indicates that either another reaction mechanism takes place on LSCo50 than on the other cobaltites or that the dissociation of oxygen or nitric oxide, or the diffusion of oxide anions through the bulk of the electrode, occurs much faster on LSCo50 than on the other perovskites. At temperatures below 400°C the cobalt-based perovskites are semiconductors, except LSCo50, which is a metallic conductor with a much higher electronic conductivity [26], and this could be the reason for the different behavior of LSCo50. There is also a change in the oxygen vacancy concentration and the electronic state of cobalt when strontium is substituted for lanthanum. This could also be the reason for the difference between LSCo50 and the other cobalt-based perovskites. A shift in reaction mechanism for LSCo50 has also been suggested on the background on a more detailed EIS study of the reduction of oxygen on cobalt-based perovskites [22]. The rate of the reduction of nitric oxide is strongly dependent on the composition of the electrode, and the rate of the reduction of nitric oxide is highest on the LSCo5 electrode at a temperature of 200°C. For other types of perovskite based electrodes it has been suggested that the redox capacity (activity) is important for the electrodes ability to electrochemically

reduce nitric oxide [9]. An electrode with a high redox capacity has the high activity towards the reduction of nitric oxide. The oxygen non-stoichiometry is zero for LSCo0 in air, and LSCo0 has only a very low redox capacity, whereas LSCo5 will have some redox capacity. The difference in activity towards the reduction of nitric oxide on LSCo0 and LSCo5 could therefore be due to differences in the redox capacity. That the activity towards the reduction of nitric oxide is lower for the higher strontium substituted cobaltites, than for LSCo0, is not clear. However, it could be due to a lower amount of Co(III) in these compounds than in LSCo5. For manganites it has also been observed that the intermediate compound LSM15 has the highest activity towards the reduction of nitric oxide [8]. This was thought to be due to a high redox capacity and oxide ion vacancies. That the activity of the cobaltite's towards the electrochemical reduction of nitric oxide increases from LSCo15 to LSCo50 could be due to the same reasons as for the electrochemical reduction of oxygen, that is an increased amount of oxide ion vacancies and an increased electronic conductivity.

Both the current density in the nitric oxide containing atmosphere and the current ratio are highest for the LSCo5 electrode, and this is therefore the most interesting cathodes for the reduction of nitric oxide in an atmosphere containing excess oxygen. LSCo5 will be further studied in an up-coming study. The current ratio of LSCo5 is on the level with the highest measured as compared with literature [13, 15-16]

Conclusion: The activity and apparent selectivity of the LSCo5 electrode towards the electrochemical reduction of nitric oxide at 200°C is the highest of the cobalt-based perovskites investigated in this study. A limiting cathodic current, in both nitric oxide and air, is observed for all the perovskites except LSCo50 at 300 and 400°C. This is probably due to a rate limiting chemical step in the reaction sequence.

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Table captions.

Table 1. Numerical current densities for all the compounds at 200, 300 and 400°C in either air or 1 % nitric oxide in argon. The current densities are given in mAcm^{-2} . The current densities increase with increasing temperature.

Table 1.

compound	LSCo0		LSCo5		LSCo15		LSCo25		LSCo35		LSCo50	
	air	NO	air	NO	air	NO	air	NO	air	NO	air	NO
200°C	0.60	0.03	0.03	0.15	0.06	0.04	0.10	0.06	0.10	0.06	0.15	0.10
300°C	15.0	1.00	1.10	5.70	1.70	1.50	2.70	0.98	1.60	0.81	6.10	3.80
400°C	24.0	24.0	9.30	18.0	3.40	5.40	8.90	7.02	11.1	5.30	750	650

Figure captions.

Figure 1. A schematic drawing of the experimental set-up. The working electrode (WE) is shaped like a cone. The electrolyte is a one end closed YSZ tube. The counter/reference electrode (CE/RE) is a porous platinum electrode. The CE/RE is exposed to air. The WE is exposed to either air or 1 % NO in Ar.

Figure 2. Voltammograms recorded on LSCo50 in air (black) or 1 % NO in Ar (red) at 200°C with a sweep rate of 1 mV/s. The current are numerically higher in air than in 1 % NO in Ar. Some hysteresis is observed in both atmospheres.

Figure 3. Voltammograms recorded on LSCo50 in air (black) or 1 % NO in Ar (red) at 300°C with a sweep rate of 1 mV/s. The cathodic currents are numerically higher in air than in 1 % NO in Ar. Some hysteresis is observed in both atmospheres.

Figure 4. Voltammograms recorded on LSCo50 in air (black) or 1 % NO in Ar (red) at 400°C with a sweep rate of 1 mV/s. The currents are almost the same in air and in 1 % NO in Ar. Some hysteresis is observed in both atmospheres.

Figure 5. Voltammograms recorded on LSCo15 in air (black) or 1 % NO in Ar (red) at 300°C with a sweep rate of 1 mV/s. A limiting cathodic current is observed in both air and 1 % NO in Ar. Some hysteresis is observed in both atmospheres.

Figure 6. Maximum numerical cathodic currents in 1 % NO in Ar at 200°C. The current is highest for LSCo5. The solid line is for optical guideline only.

Figure 7. Maximum numerical cathodic currents in air at 200°C. The current is highest for LSCo0. The solid line is for optical guideline only.

Figure 8. Current ratios at 200°C. The current ratio is highest for LSCo5. The solid line is for optical guideline only.

Figure 1.

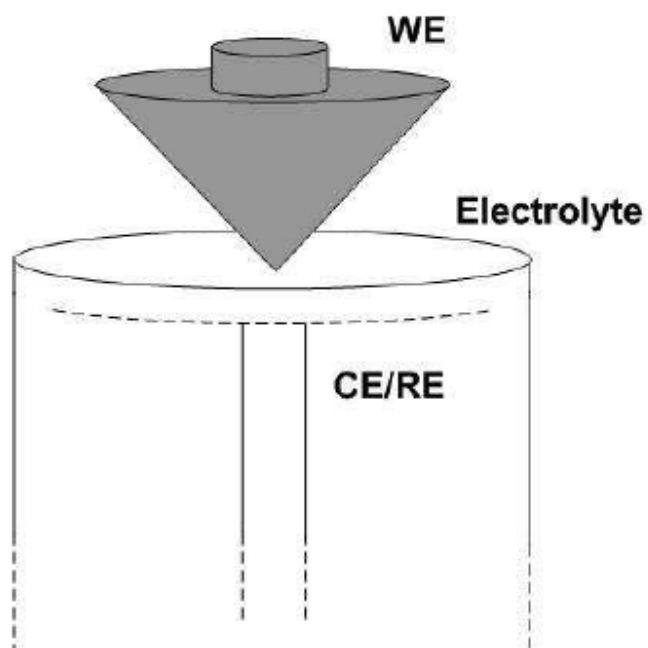


Figure 2.

LSCo50 @ 200°C

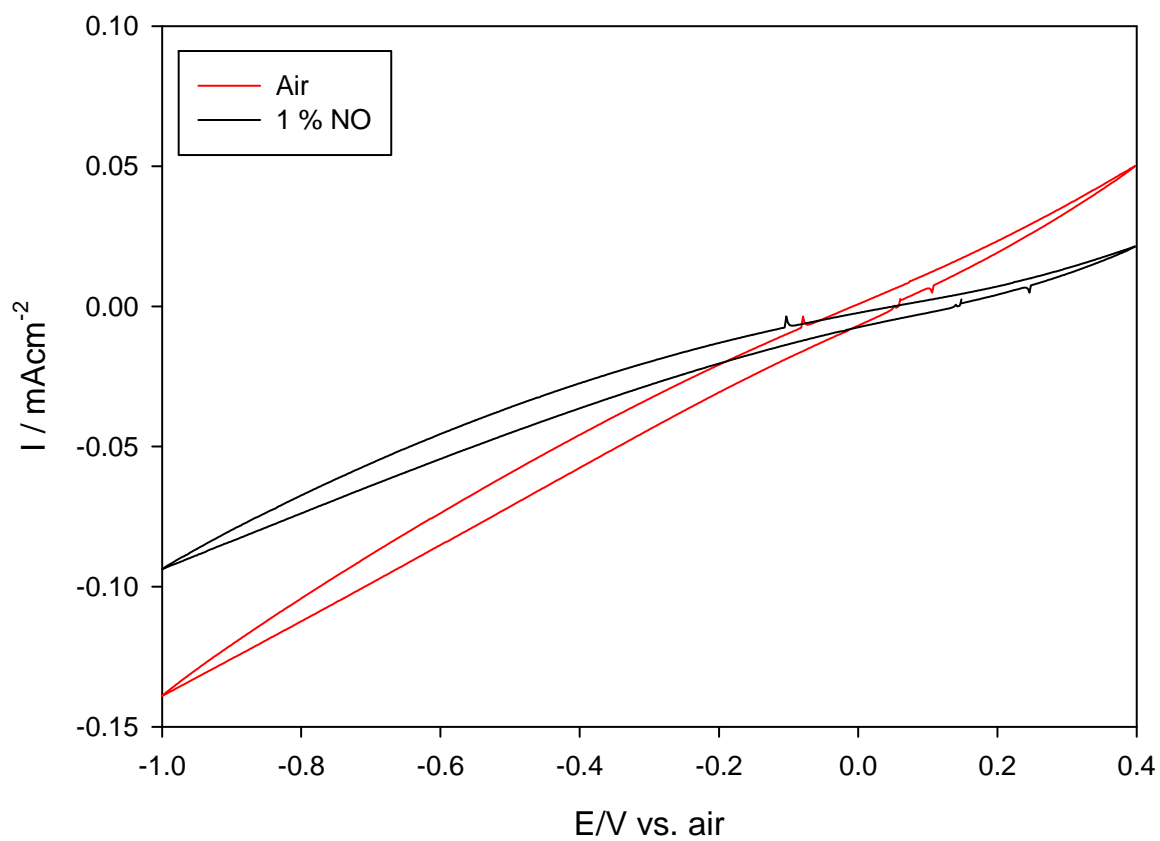


Figure 3.

LSCo50 @ 300°C

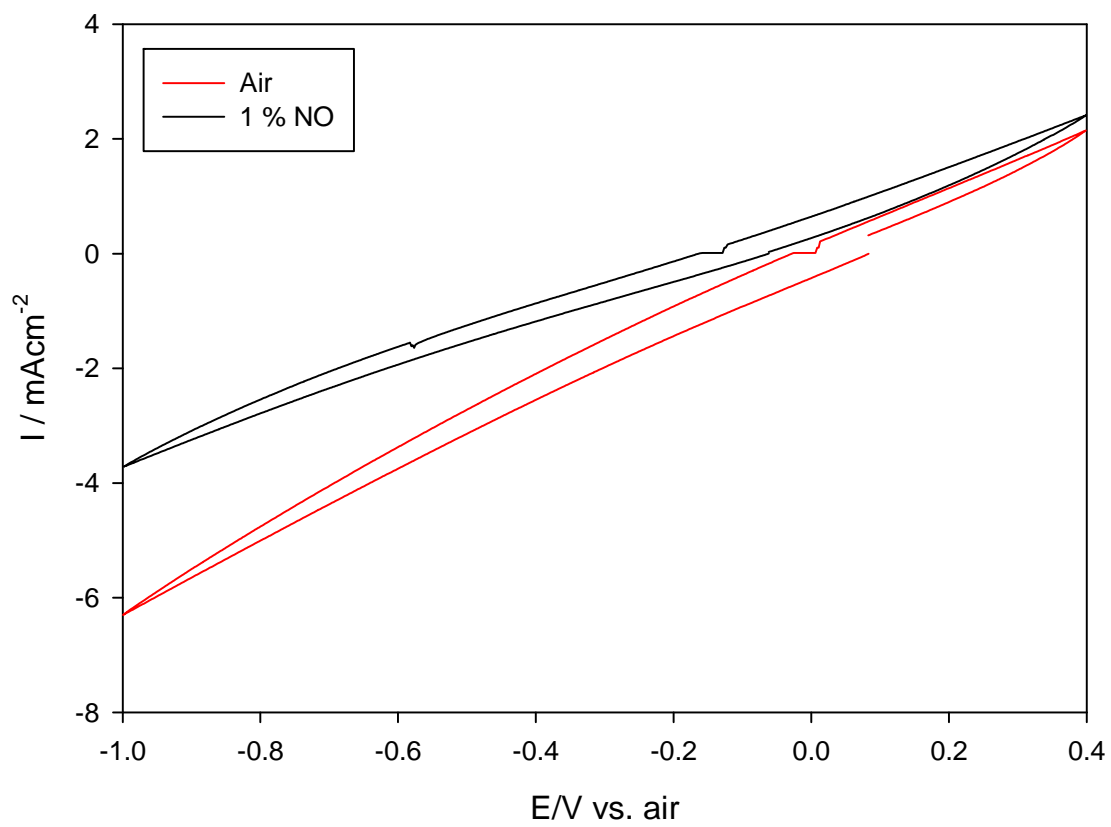


Figure 4.

LSCo50 @ 400°C

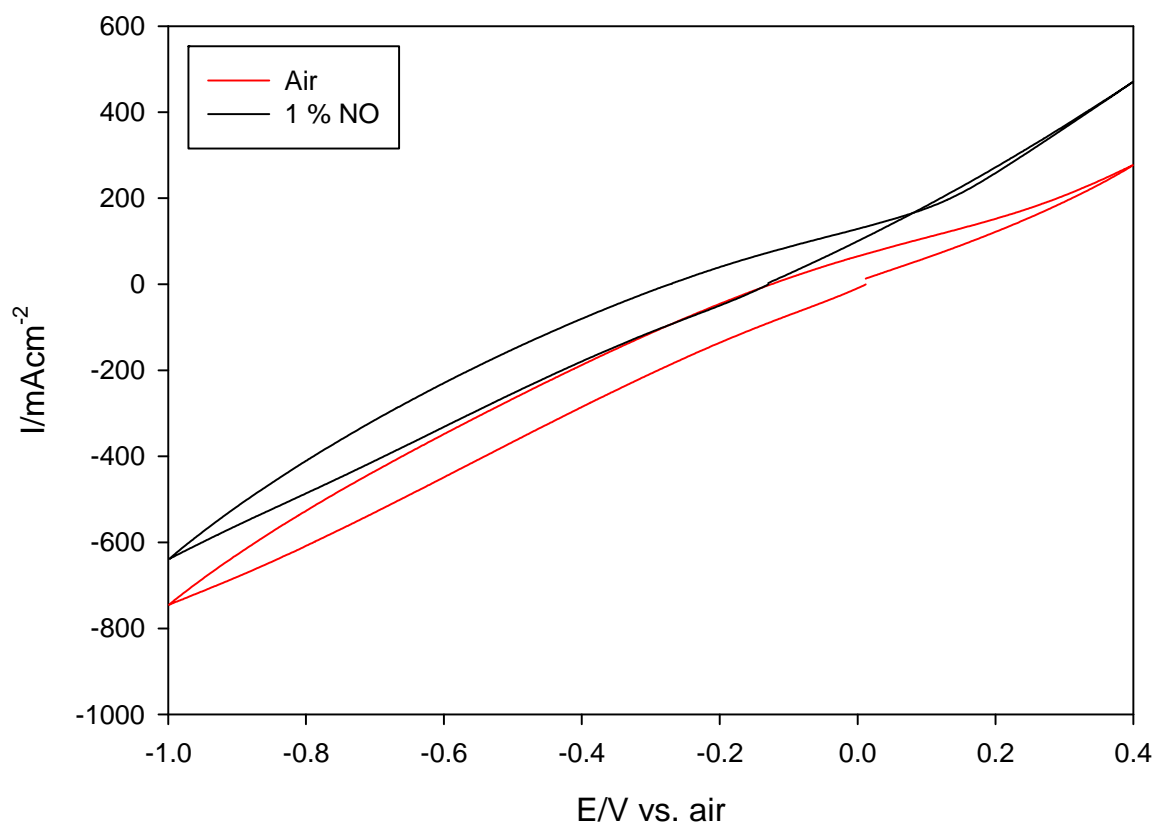


Figure 5.

LSCo15 @ 300°C

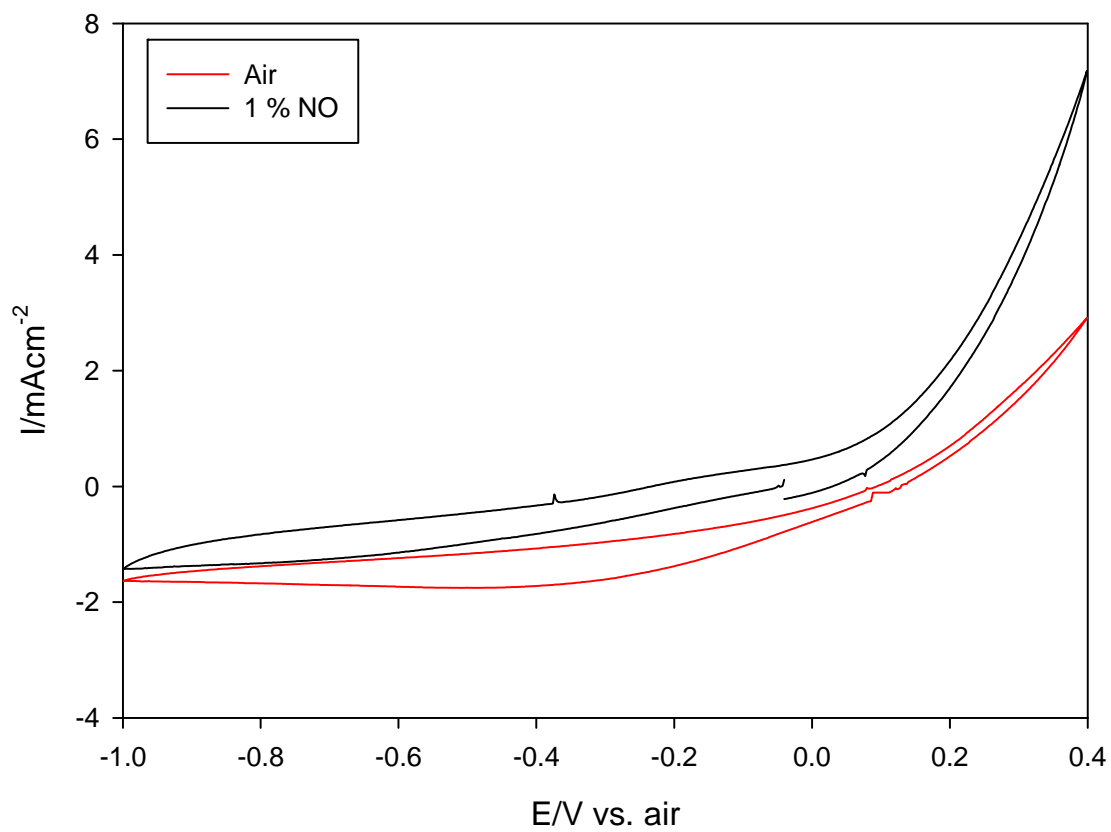


Figure 6.

LSCo @ 200°C in 1 % NO

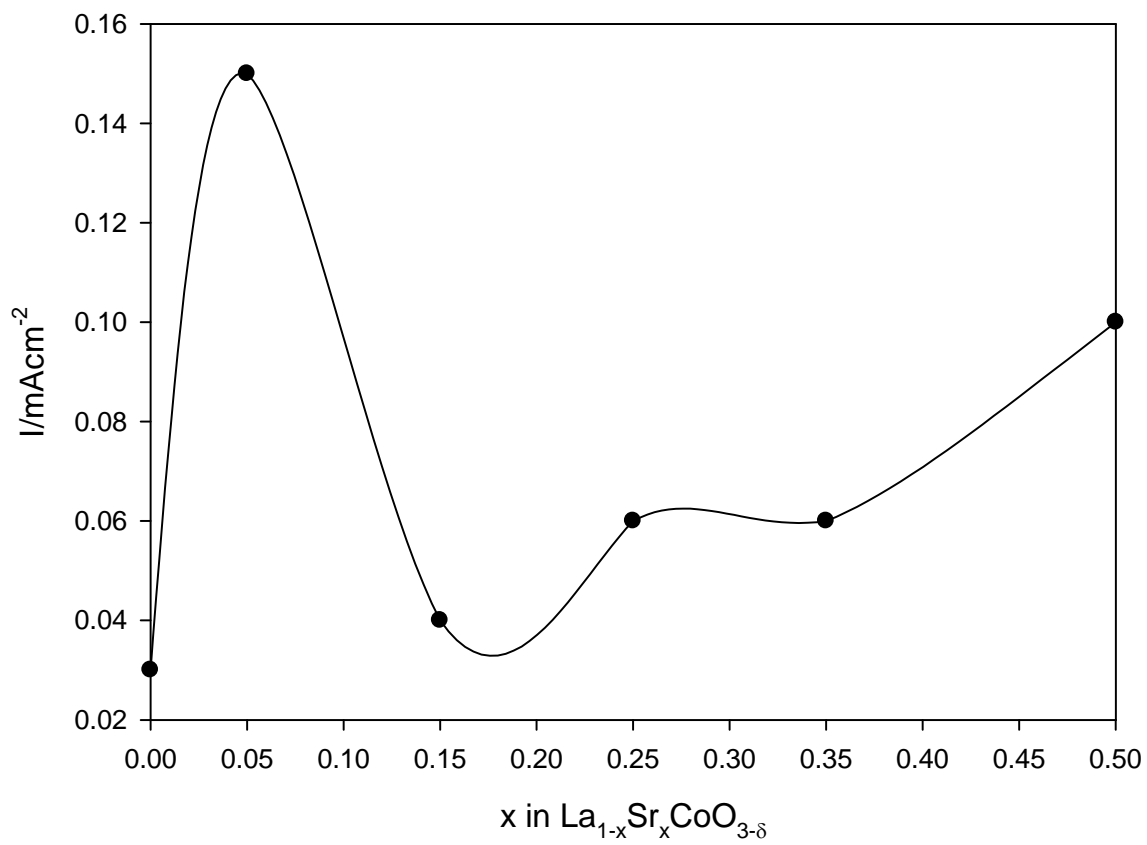


Figure 7.

LSCo @ 200°C in Air

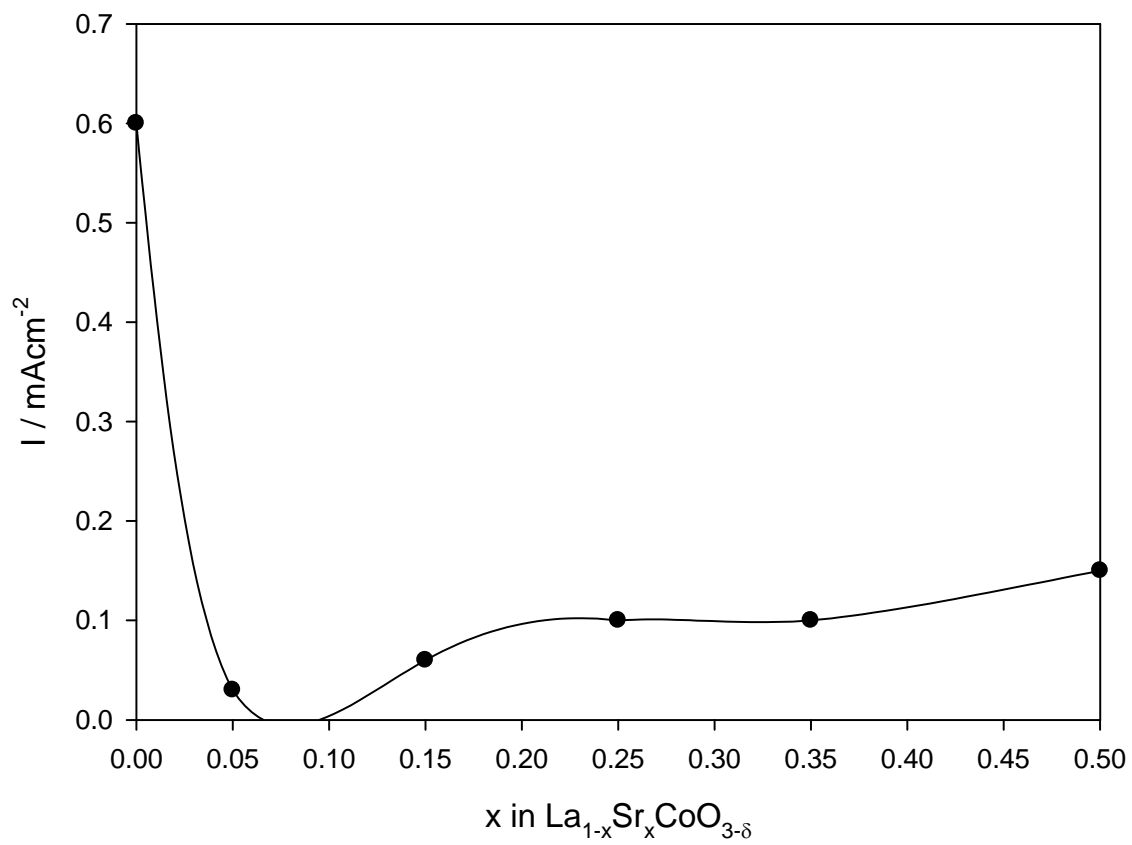


Figure 8.

Current ratios at 200°C

