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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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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 synthesized and characterized by powder X-ray diffraction and cyclic voltammetry on conical electrodes in either air or nitric oxide in argon at 200, 300, and 400°C. At 200°C, the current densities in air was the highest for the strontium-free cobaltite, whereas the current densities were the 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 cobaltites, except for $\text{La}_{0.50}\text{Sr}_{0.50}\text{CoO}_{3-\delta}$, in both air and 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.

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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 edema.² Electrochemical reduction of nitric oxide is a potentially convenient technique to remove NO_x from diesel exhaust gases.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 simultaneous reduction of oxygen at the cathode that results in a high current consumption.⁴ However, recent results have been presented in the literature that show current efficiency near 20%.⁵ The electrode used to obtain the current efficiency of 20% demands the use of an expensive noble metal in the form of platinum. The use of low cost electrodes is of outmost importance, and the search for low cost electrodes is therefore ongoing.⁶⁻¹⁶ Another problem is the activity at low temperatures in the diesel exhaust.¹⁷ Perovskites with manganite and/or iron have been studied in the literature and some of them show high apparent selectivity toward the reduction of nitric oxide in a net oxidizing atmosphere.⁷⁻⁹ However, the activity of these compounds might be too low. Among perovskites, cobalt-based perovskites show the highest activity toward 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 from 200 to 400°C on a series of cobalt-based perovskites, using conical 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 X-ray diffraction (XRD) was performed to evaluate the formation of the perovskite phase. A Stoe θ - θ diffractometer equipped with 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 conical electrodes using diamond tools. The conical electrodes were rinsed in EtOH in an ultrasonic bath before use.

The electrochemical measurements were done in a two-atmosphere setup (see Fig. 1). As an electrolyte, a one-end closed

yttria stabilized zirconia (YSZ) tube (Vesuvius) was used. The closed end of the YSZ tube exposed to the conical electrode was polished with 1 μm diamond paste before use. As a reference, gas air was used. As a counter/reference electrode (CE/RE), platinum was used. Platinum was added as a paste (Engelhard) and sintered at 1000°C/2 h in air. The setup is a pseudo-three-electrode setup, as the area of the working electrode is many times smaller than the CE/RE. 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 and -1.0 V vs air. The sweeps were initiated at open-circuit voltage (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 conical 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 six points measured per decade. An amplitude of 36 mV was used throughout.

Results

The powder XRD reveals that the synthesized cobaltites are of single phase. The cobaltites were hexagonal for $x = 0, 0.05, 0.15$, and 0.25. For $x = 0.35$ and 0.50, the cobaltites were orthorhombic. After sintering, the achieved density of the cylinders was better than 93% of the theoretical value. Examples of the voltammograms can be found in Fig. 2-5. 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 are presented. In Fig. 2, the voltammograms of the reduction of oxygen and nitric oxide at 200°C on LSCo50 are 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 mA cm^{-2} in air and -0.09 mA cm^{-2} in the nitric oxide-containing atmosphere. The reduction of oxygen and nitric oxide is initiated at almost the same potential, ~ 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 bends downward) 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 Fig. 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 oxide-containing atmosphere. The maximum current density in air is around -6 mA cm^{-2} , whereas it is around -4 mA cm^{-2} in the nitric oxide-containing atmosphere. The hysteresis observed in the figure is capacitive in both atmospheres. In Fig. 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

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Figure 1. Schematic drawing of the experimental setup. The working electrode (WE) is conical. The electrolyte is a one-end closed YSZ tube. The 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.

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 cobaltites, except for LSCo50, in both air and the nitric oxide-containing atmosphere. In Fig. 5, the voltammograms recorded on LSCo15 in air and nitric oxide at a temperature of 300°C are plotted. The maximum cathodic current densities are almost the same in air and the nitric oxide-containing atmosphere. This is observed for all the cobaltites that exhibit the behavior with a limiting current density, except for LSCo0. The behavior 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 Fig. 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 mA cm⁻². From LSCo5 to

Figure 2. (Color online) 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 is numerically higher in air than in 1% NO in Ar. Some hysteresis is observed in both atmospheres.

Figure 3. (Color online) 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.

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 are plotted in Fig. 7. The highest current densities in the nitric oxide-containing atmosphere at 200°C are found for LSCo5. The current ratios ($I_{\text{NO}}/I_{\text{O}_2}$) at 200°C are given in Fig. 8. LSCo5 is seen to have the highest current ratio at 200°C, as the current is almost a factor of 5 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 in Table I. 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 the activity toward the reduction of oxygen increases with increasing strontium content.²² This can be attributed to the increased amount of oxide ion vacancies and a higher electronic conductivity for the strontium-

Figure 4. (Color online) 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. (Color online) 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.

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 leads to more oxide ion vacancies on the surface of the electrodes. The 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 the oxidation of nitric oxide to nitrogen dioxide and the 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 ob-

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.

served 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 is first initiated below the potential where the reduction of oxygen is initiated. The reduction of nitric oxide is therefore always 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 therefore depends 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 was 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 for 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 elec-

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

Table I. 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 mA cm⁻². The current densities increase with increasing temperature.

Compound <i>T/Gas</i>	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

tronic 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 the 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, the redox capacity (activity) is important for the electrode's ability to electrochemically reduce nitric oxide.⁹ An electrode with a high redox capacity has a high activity toward the reduction of nitric oxide. The oxygen nonstoichiometry is zero for LSCo0 in air, and LSCo0 has only a very low redox capacity, whereas LSCo5 has some redox capacity. The difference in the activity toward the reduction of nitric oxide on LSCo0 and LSCo5 could therefore be due to the differences in the redox capacity. That the activity toward 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 toward 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 cobaltites toward 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 cathode for the reduction of nitric oxide in an atmosphere containing excess oxygen. LSCo5 will be further studied in an upcoming study. The current ratio of LSCo5 is on the level with the highest measured as compared with the literature.^{13,15,16}

Conclusion

The activity and apparent selectivity of the LSCo5 electrode toward the electrochemical reduction of nitric oxide at 200°C are 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 for LSCo50 at 300 and 400°C. This is probably due to a rate-limiting chemical step in the reaction sequence.

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