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Abstract The series $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ ($x=0.0, 0.05, 0.15, 0.25, 0.35$ and 1.0) was tested for the functionality as electrode materials for direct electrochemical reduction of NO. The materials were tested using cyclic voltammetry in 1% NO and 10% O_2 in Ar on a cone-shaped electrode. The best materials for the electrochemical reduction of NO are La_2NiO_4 and LaSrNiO_4 which have current densities for NO reduction 1.82 and 7.09 times higher, respectively than for O_2 at 400 °C. Increasing the temperature decreased the ability to reduce NO before O_2 while the activity increased. The adsorbed species during direct decomposition was attempted clarified using x-ray absorption near edge structure (XANES) experiments and thermogravimetry, but no conclusive results were obtained.

Keyword: Electrochemical reduction, NO, cone-shaped electrodes, K_2NiF_4 structure, $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$

1 Introduction

Due to increased environmental concerns and stricter emission regulations there is a need for new methods of removal of e.g. NO_x [1]-[2]. At the moment none of the existing technologies are able to meet the permit values for NO_x stated for 2008 [3]. Therefore new ways of NO_x -removal are under development and one of them is electrochemical reduction of NO - initially discovered by Pancharatnam et al. in 1975 [4]. Through this approach NO can be reduced in an all solid state electrochemical cell using an oxide ion conductor as the electrolyte. NO is converted to N_2 and O_2 as shown in the following equations:

The drawback of this method is the ability of the cathode to reduce O_2 alongside the reduction of NO as shown in equation 1. This side reaction only moves oxygen from one side of the cell to the other under consumption of current and thus decreases current efficiency. Thus the main challenge

within this method is to find selective materials which only reduce NO and act as catalysts for reaction 1. This study investigates $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ ($x = 0, 0.05, 0.15, 0.25, 0.35$ and 1.0) compounds as possible cathode materials for selective electrochemical reduction of NO. $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ has the K_2NiF_4 structure and has been studied for direct decomposition of NO by Zhao et al. in 1996 [5]. To our knowledge no investigations on this type of materials as a selective electrode for electrochemical reduction of NO, have been carried out.

2 Experimental Procedure

A $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4-\delta}$ series was synthesized using the citric acid synthesis described by Rao et. al. [6]. In short, metal nitrate aqueous solutions of the anticipated concentrations were mixed with citric acid and after evaporation until a viscous solution, ethylene glycol was added and the mixture was heated further. The solution did not react fully and consisted of a mixture of both solid ash and unreacted gel. Therefore, the mixture was heated in a furnace at $300\text{ }^\circ\text{C}$ for 4 h with ramps of $50\text{ }^\circ\text{C/h}$ to complete the reaction. The resulting dark ceramic powder was ball milled for 24 h before being calcined at $1100\text{ }^\circ\text{C}$ for 6 h. Phase purity and structure of the materials were checked using x-ray diffraction (XRD) on a STOE Theta - Theta diffractometer in combination with the ICDD database. The diffractograms were collected at $20\text{ }^\circ \leq 2\theta \leq 80\text{ }^\circ$, stepsize 0.05° with CuK_α radiation. The materials with $x=0.35$ and $x=1.0$ were not phase pure and were re-calcined for 6

h at 1200 °C and 1300 °C, respectively. Even after treatment at 1300 °C, LaSrNiO_4 was not completely single phased and contained approximately 1% of Sr-impurities.

After phase purity was obtained the powder was uniaxially pressed to pellets in an appropriate mould, isostatically pressed at 1 ton and sintered at 1250 °C for 12 h. The pellets were machined into cone-shaped electrodes (base diameter 7.5 mm and side angles 45 °) with a diamond tool. Before any measurements were conducted on electrodes, they were subjected to an ultrasonic bath for 20 min in ethanol to remove any remains in form of oil and metallic splinters from the mechanical tooling.

When investigating the ability of the $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4-\delta}$ materials for electrochemical reduction of NO, a pseudo three electrode setup was used as described by Hansen et. al. [8]. The setup was an all solid state electrochemical setup, with the working electrode being the in-house produced cone-shaped electrode described above. This setup is used as the influence from microstructure on the results are minimized due to the small contact area and the method allows quick analysis of many different materials. The cone-shaped electrode was pressed against an electrolyte of yttria stabilized zirconia (10.5% YSZ) with 60 g of weights. The combined counter- and reference electrode was silver paste (Ferro, 6122 0002) applied onto the YSZ and exposed to an air atmosphere. All potentials given in this study are re-

ported vs. air. Furthermore, the counter/reference electrode was connected with a Pt/PtRh thermocouple which enabled monitoring the true temperature of the setup.

During experiments the working electrode was subjected to 1% NO in Ar (certified to $\pm 2\%$ from Air Liquide) or 10% O_2 in Ar from Air Liquide. The reason for the choice of these different concentrations, is that the concentration of O_2 in the exhaust gas from lean burn Otto engines is approximately 10 times higher than that of NO. Brooks mass flow controllers were used to control the flow which was kept at 25 ml/min and the temperature of the furnace was controlled by a Eurotherm temperature controller.

To determine the conversion of nitric oxide or oxygen, cyclic voltammograms (CV) were recorded in the potential range -0.5 V to 0.5 V vs. Ag/air as the resulting current responses were directly proportional to the conversion. All cycles are initiated from open circuit voltage (OCV) and run in the direction of negative overpotential before sweeping in the positive overpotential region. As the tip area of the electrode differed from electrode to electrode, the contact area between the cone-shaped electrode and electrolyte was determined by electrochemical impedance spectroscopy (EIS) measurements in combination with Newman's formula (equation 1) [9]. The impedance spectra were recorded on a Solartron 1255b + 1287, frequency analyzer (range 0.05 Hz - 700 kHz, 20 points per decade and an amplitude

of 25 mA) and used to determine the value of R_s .

$$r = \frac{1}{4\sigma R_s} \quad (1)$$

Newman's formula assumes that the contact area is circular and r is the radius of the contact area in cm, σ is the specific conductivity of the electrolyte material given in S/cm and R_s is the electrolyte resistance in Ω . The specific conductivity of the electrolyte material as a function of temperature can be determined from Appel et. al. [10]

Newman's formula assumes that the contact area is circular, which is not entirely accurate but scanning electron microscopy images show that the calculated contact area is fairly accurate. All currents obtained in the CVs were normalized to current densities to make a direct comparison the materials possible.

X-Ray Absorption Near Edge Structure (XANES) experiments were carried out on beamline E4 at HASY LAB, DESY, Hamburg, Germany. A homemade setup was used for the in-situ XANES experiments described in this study [14]. A pellet containing 5 mg sample and 45 mg Al_2O_3 was pressed in a 10 mm mould. The pellet was placed horizontally in a glass tube, with Kapton windows in the ends to allow radiation to pass and it was possible to change the atmosphere around the sample. The glass tube was placed in a furnace and heated to 496 °C in air. After 2 measurements at constant temperature, the atmosphere was changed to 1% NO in Ar and

left for 3 h to measure reproducible XANES spectra. The atmosphere was changed back to air prior to cooling down the furnace. XANES spectra were recorded repeatedly, the recording time of a spectrum was approximately 20 min.

The data was analyzed using the Athena analysis software [15]. After subtracting the background, the spectra for La_2NiO_4 and LaSrNiO_4 in 0.5% NO at 496 °C were modeled to the best fit from a linear combination of La_2NiO_4 and LaSrNiO_4 in air and at room temperature as no standards for Ni^{2+} and Ni^{3+} in the K_2NiF_4 structure exist. From thermogravimetric experiments the oxygen stoichiometry and thus amount of Ni^{2+} and Ni^{3+} of the two compounds at room temperature in air was determined by reducing a sample completely in 9% H_2 in N_2 . The linear combination allows us to determine the amount of Ni^{2+} and Ni^{3+} of the samples at 496 °C in 0.5% NO.

Thermogravimetric (TG) experiments were conducted on a Seiko 320 TG using alumina crucibles and a reference weigh of alumina and gold. The temperature and gas composition was varied and the actual partial pressure of O_2 was determined using a homemade oxygen sensor consisting of an electrochemical cell which measured the OCV continuously through out all experiments. At 496 °C the sample was subjected to 1% NO and the weight gain and oxygen partial pressure was noted. NO is known as a reducing gas and the oxygen sensor measures a value of ($p_{\text{O}_2} = 0.00038$ atm).

The equivalent p_{O_2} created from air and N_2 was subjected to the sample to determine the actual adsorption of NO.

3 Results and Discussion

The electrochemical measurements were carried out at 400 °C, 500 °C and 600 °C, respectively. The exhaust in a diesel engine is approximately 350 °C, but as oxide ion conductivity in YSZ is too low at temperatures below 400 °C we cannot measure at that temperature. It should be noted that the measure for an applicable material is not only the ability to reduce NO compared to O_2 but also the activity of the electrode towards NO reduction. Therefore the best material is a result of a trade off between activity of the electrode material and the ability to reduce nitric oxide before oxygen.

3.1 Electrochemical Reduction of NO and O_2

The series of materials is tested using cyclic voltammetry and a typical cyclic voltammogram is shown for LaSrNiO_4 in figure 1. Figure 1 shows that at approximately -100 mV the electrode is better at reducing NO than O_2 . The larger the negative overpotential becomes, the larger the numerical current densities are seen for NO whereas the reduction of O_2 is only effected slightly. Under anodic conditions oxygen ions will be pumped through the electrolyte and thus the final product in the reaction gas can be either NO_2 or O_2 . In the reaction gas containing O_2 the only product in the oxidizing region can be O_2 but in NO the current initiates at lower potentials than

the in the O_2 reaction gas. This could indicate that the product in the NO reaction gas is NO_2 or a mixture of NO_2 and O_2 , where the catalytic activity of the electrode material is higher for NO_2 formation than O_2 formation. Unfortunately the gas conversion over the cone-shaped electrode is so low that it is not possible to measure and thus confirm the formation of either NO_2 , O_2 or a mixture of the two by gas analysis. Figure 2 shows the current densities obtained at -0.5 V at 400 °C of O_2 and NO reaction gas as a function of Sr-content. The optimal electrode material will have numerically high current density for NO reduction and low numerical current densities for O_2 . The optimal composition will always be a trade off between numerical high current densities and ratio between the two current densities. As seen from figure 2 the two compounds which meet these requirements best are La_2NiO_4 and LaSrNiO_4 . La_2NiO_4 and LaSrNiO_4 exhibit the highest numerical current densities for NO while the ratio is highest for LaSrNiO_4 . High ratios are also observed for $x=0.15$ and $x=0.35$, but these materials do not exhibit high current densities and thus La_2NiO_4 and LaSrNiO_4 are found to be the two most promising materials. The ratio between current densities for NO and O_2 at 400 °C, 500 °C and 600 °C are summarized in table 1. An interesting effect is shown for $x=0.05$ which exhibits high numerical current densities for O_2 and NO reduction but the effect disappears when the Sr-content is increased. Furthermore, the ability to reduce O_2 is approximately 5 times higher for the O_2 reduction than NO reduction, so the material is of no real interest in this specific research area. The experiment

was reproduced with the same result. The experiment also showed that increasing the temperature increased activity in the form of current densities but the ratio of NO vs. O₂ reduction decreased with increasing temperature.

The two most promising materials tested in the series were $x=0.0$ and $x=1.0$. Thermogravimetric experiments conducted on these materials show that the oxygen stoichiometry is La₂NiO_{4.17} and LaSrNiO_{3.9}, respectively. Kammer Hansen et al. [11] proposed the oxygen stoichiometry of perovskites to influence the ratio between activity of the nitric oxide over oxygen reduction reaction. For the series of materials in this study, no direct relation between the oxygen vacancies and the NO/O₂ activity ratio is seen. The K₂NiF₄ structure consists of perovskite layers with alternating layers of MeO. Thus the properties of the K₂NiF₄ structures could be assumed to follow the properties of the perovskite structure which is not the case as the two best materials in this study have interstitial oxygen and oxygen vacancies, respectively. In 1996, Zhao et al. [12] tested a series consisting of LaNiO₃, La_{0.9}Sr_{0.1}NiO₃, La₂NiO₄ and LaSrNiO₄ for the direct reduction of NO. They reached the conclusion that the redox capacity (the ability for the transition metals to change oxidation state within the structure) and oxygen vacancies were the most important factors in direct decomposition of NO and that a high content of Ni²⁺ is favorable for the direct decomposition of NO. This is in agreement with what was found by Kammer Hansen et al. [11] for perovskites who also stated that redox activity and amount

of Ni^{2+} to have an effect on the ratio between activities on the reduction of NO vs. O_2 . Zhao et. al. [12] hardly found any activity but high selectivity for $\text{La}_2\text{NiO}_{4+\delta}$, and they attributed high concentration of Ni^{2+} to be the active site for NO decomposition. In this study we see a high activity in $\text{La}_2\text{NiO}_{4+\delta}$, which could be due to interstitial oxygen which could be more easily mobilized due to electrochemical manipulation. Through temperature programmed desorption experiments Zhao et. al. [12] found that the oxygen vacancies were disordered in LaSrNiO_4 . Disordering of oxygen vacancies have been reported an important factor for activity of direct reduction of NO for similar compounds such as e.g. $\text{YBa}_2\text{Cu}_3\text{O}_{7+\delta}$ [13].

3.2 Adsorbed Species During Reduction

Numerous species have been suggested as intermediates in the direct reduction of NO [18] - [34]. In common for all the suggested intermediates is the fact that NO binds to the B atom in the perovskite, ABO_3 and the similar K_2NiF_4 -structure, A_2BO_4 . The missing electrochemical studies are probably due to the difficulty in conducting in situ surface species measurements during electrochemical measurements. In this study direct decomposition measurements were carried out using X-Ray Absorption Near Edge Structure (XANES) and thermogravimetry (TG). The principle behind the experiments was to investigate the oxidation state of Ni when 0.5% NO is subjected to some of the sample material by using XANES. The results from XANES showed that Ni^{3+} ions were reduced when NO was subjected to the

$\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ sample, which was expected as NO is a reducing gas. Figure 3 shows the difference in XANES spectra when the LaSrNiO_4 sample is subjected to air at room temperature, at 496 °C in air and NO, respectively, and when the sample is cooled to room temperature in air again. As seen from figure 3, the sample is oxidized when heating, which is presumed to be due to the preparation procedure and thus the sample takes up oxygen upon heating. When the sample is subjected to NO, the sample is visibly reduced also beyond the extent of the initial oxidation state. The sample does not reach the original oxidation state in air, but the is not expected as the sample is semi-quenched when cooling.

The concentrations of Ni^{2+} and Ni^{3+} ions for $x = 0$ and 1 is given in table 2. Investigating the weight loss in TG can give an idea of the reduction capacity of NO in the material. Single phased materials were assumed but even the 1% impurities present in LaSrNiO_4 will not influence the calculated $\text{Ni}^{2+}/\text{Ni}^{3+}$ ratio to a significant extent. Combining the result of the two measuring techniques was believed to give detailed information on the charge of the adsorbed species. As NO is a reducing gas the equivalent p_{O_2} was subjected to the sample by mixing N_2 and air in the TG. The result of the measurements suggests that NO was adsorbed as an NO^- -species on the surface of La_2NiO_4 and LaSrNiO_4 . The change in amount of Ni^{2+} is from 65.6% to 64.6% and 25.9% to 23.1% for $x = 0.0$ and $x = 1.0$, respectively. Thus we would expect the NO molecules to sit on every 100th and

30th Ni atom. Subjecting the samples to 1% NO in TG showed that NO was adsorbed on every 60th and 130th Ni-atom, respectively. This shows that the data is not in agreement which is most likely due to the fact that we are comparing measurements in the uncertainty range of the XANES measurements. The XANES measurements are carried out with a stepsize in radiation of 0.02 eV resulting in measurable changes of 5-10% Ni-ion concentration changes. Another possibility is that the adsorbed molecule is not an NO-species but perhaps an NO_2 -species on one of the materials. Zhao et al. [12] reported a shift in reaction mechanism for the NO reduction on La_2NiO_4 and LaSrNiO_4 , respectively, which could be due to different adsorbed species. It would be very interesting to verify the charge of adsorbed NO using IR spectroscopy or a similar technique.

4 Conclusion

Electrochemical reduction of NO and O_2 was carried out on a series of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$. The best performances on basis of activity of the electrode materials and NO vs. O_2 conversion were obtained on La_2NiO_4 and LaSrNiO_4 . Of these two, LaSrNiO_4 had higher ratios between NO and O_2 reduction most likely due to the high concentration of oxygen vacancies and the redox pair of $\text{Ni}^{2+}/\text{Ni}^{3+}$. Thus LaSrNiO_4 is seen as the most promising material for future study.

No conclusions could be drawn in respect to the determination of the ad-

sorbed species. XANES in combination with TG led to ambiguous results due to the fact that the uncertainty of the XANES measurements was larger than the effects observed.

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References

1. www.dieselnet.com/standards/eu/hd.html (2006)
2. www.dieselnet.com/standards/eu/ld.html (2006)
3. Klingstedt F, Arve K, Ernen K, Murzin DY (2006) *Acc Chem Res* 39:273
4. Pancharatnam S, Huggins RA, Mason DM (1975) *J Electrochem Soc* 122:869
5. Zhao Z, Yang XG, Wu Y (1996) *Chem Research in Chinese Universities* 1:81
6. Rao KK, Banu T, Vithal M, Swamy GYSK, Kumar KR (2002) *Mater Lett* 54:6

7. Chick LA, Pederson LR, Maupin GD, Bates JL, Thomas LE, Exarhos GJ (1990) *Mater Lett* 10:6
8. Hansen KK, Christensen H, Skou EM, Skaarup SV (2000) *J Appl Electrochem* 30:193
9. Newman J (1966) *J Electrochem Soc* 113:501
10. Appel CC, Bonanos N, Horsewell A, Linderroth S (2001) *J Mater Sci* 36:4493
11. Kammer Hansen K, Skou EM, Christensen H (2000) *J Electrochem Soc* 147:2007
12. Zhao Z, Yang Y, Wu Y (1996) *Appl Catal, B* 8:281
13. Alario-Franco MA, Chaillout C, Capponi JJ, Chenavas J (1987) *Mater Res Bull* 22
14. Hagen A, Schueler K, Roessner F (2002) *Microporous Mesoporous Mater* 51:23
15. Ifettit, Athena - version 0.8.050 (2001-2006) Bruce Ravel
16. Zhen Z, Xiangguang Y, Yue W (1996) *J Rare Earths* 14:241
17. Turco RP (1997) *Earth under Siege - from Air Pollution to Global Change*. Oxford University Press
18. Jellinek K (1906) *Anorg Z u Allgem Chem* 49:229
19. Hightower JW (1975) *The Catalytic Chemistry of Nitrogen Oxides: Current Status of the Catalytic Decomposition of NO*. Plenum Press, NY
20. Winter ERS (1971) *J Catal* 22:158

21. Shin S, Arakawa H, Hatakeyama Y, Ogawa K, Shimomura K (1979) Mater Res Bull 14:633
22. Shelef M, Kummer JT (1970) Chem Eng Progress Symposium Series 67:74
23. Shelef M (1992) Catal Lett 15:305
24. Xie S, Mestl G, Rosynek M, Lunsford J (1997) J Am Chem Soc 119:10186
25. Mestl G, Rosynek M, Lunsford J (1997) J Phys Chem 101:9329
26. Zhu J, Zhao Z, Xiao D, Li J, Yang X, Wu Y (2005) Electrochem Commun 7:58
27. Zhu Z, Xiao D, Li J, Xie X, Yang X, Wu Y (2005) J Mol Catal A: Chem 233:29
28. Ishihara T, Ando M, Sada K, Takiishi K, Yamada K, Nishiguchi H, Takita Y (2003) J Catal 220:104
29. Haneda M, Tsuboi G, Nagao Y, Kintaichi Y, Hamada H (2004) Catal Lett 97:145
30. Haneda M, Kintaichi Y, Hamada H (2005) Appl Catal, B 55:169
31. Tofan C, Klvana D, Kirchnerova J (2002) Appl Catal, A 223:275
32. Tofan C, Klvana D, Kirchnerova J (2002) Appl Catal, A 226:225
33. Zhu J, Xiao D, Li J, Yang X, Wu Y (2005) J Mol Catal A: Chem 236:182
34. Amirnazmi A, Boudart M (1975) J Catal 39:383

Table 1 Ratios of the current densities i_{NO} over i_{O_2} for the $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ series at 400 °C, 500 °C and 600 °C.

Compound	400 °C	500 °C	600 °C
$x = 0$	1.82	1.08	0.744
$x = 0.05$	0.173	0.010	0.163
$x = 0.15$	2.14	2.21	0.659
$x = 0.25$	1.58	1.32	0.727
$x = 0.35$	3.16	1.08	1.14
$x = 1.0$	7.09	1.62	0.348

Table 2 Content of Ni^{2+} and Ni^{3+} in TG and XANES measurements for $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$, $x = 0, 1$ at 496 °C and 1% NO in Ar for the XANES measurements and $p_{\text{O}_2} \sim 1\%$ NO in Ar for TG.

Compound	XANES		TG	
	Ni^{2+}	Ni^{3+}	Ni^{2+}	Ni^{3+}
La_2NiO_4	0.65	0.35	0.66	0.34
$\text{La}_{1.0}\text{Sr}_{1.0}\text{NiO}_4$	0.23	0.77	0.26	0.74

Fig. 1 Cyclic voltammograms obtained for LaSrNiO_4 electrode at 400 °C. The measurements are performed in 10% O_2 in Ar and 1% NO in Ar at 1 mV/s.

Fig. 2 Current densities obtained at -500 mV and 400 °C for the La_2NiO_4 series.

The measurements are performed in 10% O_2 in Ar and 1% NO in Ar.

Fig. 3 The XANES spectra obtained on a sample of LaSrNiO_4 at room temperature in air, after heating to 496 °C, at 496 °C after the atmosphere is switched to NO, and after the sample has been cooled to room temperature in air.