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An EIS study of $La_{2-x}Sr_xNiO_{4+\delta}$ SOFC cathodes.

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Abstract: $La_{2-x}Sr_xNiO_{4+\delta}$ materials were investigated as cathodes for the electrochemical reduction of oxygen on a $Ce_{1.9}Gd_{0.1}O_{1.95}$ (CGO10) electrolyte using cone-shaped electrodes together with electrochemical impedance spectroscopy (EIS). The area specific resistance (ASR) of the $La_{2-x}Sr_xNiO_{4+\delta}$ nickelates towards the reduction of oxygen is equal to the ASR of perovskites; however, not as low as for the best Fe-Co based perovskites. The lowest ASR is found for the compound $La_{1.75}Sr_{0.25}NiO_{4+\delta}$ with an ASR of 23.8 Ωcm^2 measured on a cone-shaped electrode in air at 600^oC. It is suggested that difference in oxide ionic conductivity of the nickelates is the main cause for the different activity of the nickelates towards the electrochemical reduction of oxygen.

Introduction: Environmental friendly production of heat and electricity is highly desirable. One way to achieve this is the use of a solid oxide fuel cell (SOFC) [1]. However, one major obstacle that must be overcome before commercialisation of the SOFC is a lowering of the operation temperature [2]. In order to make this possible new electrode materials are needed. On the cathode side several alternatives exist to

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the classical LSM/YSZ (LSM = Strontium substituted Lanthanum Manganite, YSZ = Yttria Stabilised Zirconia) SOFC cathode. Among the alternative cathodes Co and Fe-Co based perovskites reveal the highest activity towards the reduction of oxygen [3]. However, an alternative to perovskite based cathodes could be nickelates with the K_2NiF_4 structure [4, 5]. It has been shown that the nickelates has an activity in the same order of magnitude as manganese based perovskites [4, 5]. In this work a series of $La_{2-x}Sr_xNiO_{4-\delta}$ nickelates (x = 0.00, 0.05, 0.15. 0.25 and 0.35) are synthesised and investigated using the cone-shaped electrode technique together with EIS. The cone-shaped electrode technique is a convenient method when different electrode materials are to be compared. The use of point (or cone-shaped) electrodes were first suggested by *Fabry and Kleitz* [6]. As the name indicates the working electrode is shaped like a cone, and the cone-shaped electrode is pushed towards the electrolyte with a small weight.

Experimental: Synthesis of the nickel based materials was done using the glycine-nitrate route [7]. In short the metal-nitrates dissolved in water were mixed in the appropriate ratio in a beaker, before glycine was added. The mixtures were then heated on a hot plate until combustion. The resulting powders were then transferred to alumina crucibles and the powders were calcined at $1100^oC/12$ h in air in a box furnace. The metal nitrates used were the following: $La(NO_3)_3 \bullet 6H_2O$ (Alfa Aesar, 99.9 %), $Sr(NO_3)_2$ (Alfa Aesar, 99 %) and $Ni(NO_3)_2 \bullet 6H_2O$ (Fluka, 97 %). After calcination the powders were investigated with powder X-ray diffraction (XRD) using a Stoe theta-theta diffractometer equipped with $Cu_{k\alpha}$ radiation. The cone-shaped electrodes were made as follows: 7-8 g of powder was pressed in a die with diameter = 10 mm. Thereafter the cylinders were sintered at 1250^oC in air in a box furnace for

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12 h. Finally the cylinders were machined into cone-shaped electrodes by the use of diamond tools. As an electrolyte a pellet of CGO10 (Rhodia) was used. The CGO10 pellets were made by mixing CGO10 powder with stearic acid and glycerine (both 1 w/w %) in a ball mill together with EtOH. The mixture was ball milled overnight. After drying the mixture was pressed into pellets. The pellets were sintered at $1500^{o}C/2$ h in air in a box furnace. After sintering the pellets were polished with diamond paste (1 μm). The thickness of the electrolyte pellets were around 2-3 mm. The electrochemical measurements were done in a set-up described in [8]. The EIS measurements were done using a Solartron 1260 in stand alone mode. The electrochemical measurements were done at temperatures of 800, 700 and $600^{o}C$ in air. Before the measurements the cone-shaped electrodes were equilibrated at each temperature for 24 h. The EIS were recorded from 1 MHz to 0.05 Hz with five points measured at each decade. An amplitude of 24 mV were used throughout. The PC-DOS program 'equivcrt' by B.A. Boukamp [9] was used for fitting of the data. The data were fitted with the circuit $R_s(R_1Q_1)(R_2Q_2)(R_3Q_3)$, where R is a resistance and Q is a constant phase element with the admittance:

(1) $Y = Y_0(j\omega/\omega_0)^n$,

where Y_0 is a constant, ω is the cyclic frequency, and n is an exponent. Y_0 and n is found from the fitting.

The contact area of the cone-shaped electrodes was determined by the use of Newman's formula [10]:

$$(2) \qquad r = \frac{1}{4R_s \sigma *} ,$$

where R_s is the intercept with real axis in the impedance plot at high frequency, and

$\sigma *$ is the specific conductivity of the electrolyte. r is the radius of the contact between

the cone-shaped electrode and the electrolyte, from which the contact area can be

calculated. The calculated contact areas are around 10^{-4} cm^2.

Results: The results from the powder XRD experiments reveal that all the nickelates

are of single phase [11]. All the nickelates belong to the tetragonal crystal system. The

densities of cone-shaped electrode were around 90 % of the theoretical value. An

example of an EIS spectrum can be found in Figure 1. The spectrum consists of three

arcs, as validated by the fitting using 'equivcrt'. Characteristic frequencies are

indicated on the spectrum. The total ASR values for the nickelates at 600, 700 and

800°C are listed in Table 1. The total ASR finds its minimum for the compound with

the composition $La_{1.75}Sr_{0.25}NiO_{4+\delta}$ with an ASR value of 23.8 Ωcm^2 at 600°C. The

total ASR values of the nickelates at 600°C are plotted in Figure 2. The results of the

fitting of the EIS measurements at 600°C can be found in Table 2 in the form of ASR

of the individual arcs together with the n values.

Discussion: The ASR of the investigated nickelates towards the reduction of oxygen

is on the level with good perovskite based cathodes [12-16]. This indicates that

nickelates with the K_2NiF_4 structure can be used instead of perovskite based

nickelates. However, the ASR of the nickelates is not as low as for the best Fe-Co

based perovskite materials [16]. It should be noted that the ASR found on cone-

shaped electrodes is much higher than the ASR found on planar porous composite electrodes, see i.e. [16, 17]. This is partly due to the fact that the cone-shaped electrodes not are composite electrodes, and partly due to the interface between the electrode-electrolyte, which not is optimized in the case of the cone-shaped electrodes. The geometrical configuration of the cone-shaped electrode limits the number of contact points at the electrode/electrolyte interface. Also the cone-shaped electrode is dense and therefore has a low surface area.

The interpretation of the EIS data can be done accordingly to the mechanism suggested for perovskite based electrodes by *Siebert et al.* [18] and others [19]. In this mechanism the high frequency arc is suggested to be due to transfer of oxide ions at the electrode-electrolyte interface. The near-equivalent capacity of this arc can be calculated using the following equation [20]:

$$(3) \qquad C_\omega = R^{(1-n)/n} Y_0^{1/n},$$

Where R is a resistance, and Y_0 and n is defined as in equation (1). The near-equivalent capacity of the high frequency arc is around 0.5 μFcm^{-2} for all the compounds at 600^oC, strongly suggesting that this arc is due to a double layer effect. The near-equivalent capacity is in close agreement with the value found for a double layer capacitance in [21]. The n value for this arc is about the same for all the nickelates, indicating that it is the same reaction that gives rise to this arc on the different nickelates. With respect to the magnitude of the high frequency arc in the impedance spectra no clear trend are observed for this arc with x. This could be because the magnitude of the high frequency arc depends on the micro-structure of the cone-shaped electrodes and therefore does not reflect true material properties of

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the electrode materials. The medium frequency arc seems to vary systematically with the amount of strontium in the structure as it decreases with increasing strontium content until x = 0.25 where after it increases again. That the medium frequency arc is absent for the compound with x = 0.25 is because it is not possible to separate the medium frequency arc from the low frequency arc in the fitting. No detailed study of the mechanism, for the reduction of oxygen on this type of cathode materials, has been made. However, if the same mechanism as for perovskites is valid then the medium frequency arc is due to diffusion of oxide anions in the bulk of the electrode [18, 19]. This indicates that the ionic conductivity of the $La_{2-x}Sr_xNiO_{4-\delta}$ materials find its maximum for the compound with x = 0.25 as the magnitude of the medium frequency arc is lowest for this compound. When x is increased the amount of interstitial oxygen decreases and the compound with x = 0.25 has almost no interstitial oxygen [22]. This might lead to a high mobility of oxide ions in these layers. At x = 0.35 no more interstitial oxygen is present, and the conduction of oxygen must proceed via oxide ion vacancies in the structure. For the compound with x = 0.35 only a low amount of oxide ion vacancies will be present in the structure leading to a low oxide ionic conductivity. The low frequency arc is for perovskites normally attributed to a slow redox reaction at the surface of the electrode [18, 19]. This arc decreases when x is increased from 0.00 to 0.05, and it is of approximately the same magnitude as the compound with x = 0.15. When x is further increased the magnitude of the low frequency arc increases. This indicates that the redox reaction occurs most easily on the cathodes with x = 0.05 and 0.15. This could be due to a high oxide ion conductivity of these materials. However, it does not explain why the magnitude of this arc increases when going from x = 0.15 to 0.25, where the oxide ion conductivity also increases. This indicates that another parameter plays a role in the

bond breaking of oxygen. This parameter could be the amount of Ni(II) as the amount of Ni(II) decreases with increasing x. It should be mentioned that the electronic conductivity also depends on the amount of strontium as it decreases with increasing x [11]. A lowered electronic conductivity might slow down the redox reaction. However, this can not explain why the intermediate materials are more active than the strontium poor materials, and it suggests that the electronic conductivity is of less importance for the redox reaction on this type of materials. The n values are strongly dependent on the composition of the electrode material. However, this might reflect the quality of the EIS data. The near-equivalent capacity of this arc can be calculated as for the high frequency arc. The values are given in Table 3 for a temperature of $600^{\circ}C$. The values all fall into the range depicted for a chemical capacitance in [23].

Conclusion: The $La_{2-x}Sr_xNiO_{4+\delta}$ materials have a performance equal to good perovskite SOFC cathodes. The ASR is mainly determined by the oxide ionic conductivity of the materials. The intermediate compound $La_{1.75}Sr_{0.25}NiO_{4+\delta}$ has the lowest ASR at $600^{\circ}C$.

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Table captions:

Table 1. Total ASR values for the five nickelates at 600, 700 and 800°C in air.

Table 2. ASR and n values of the individual arcs for the five nickelates at 600°C in air. High is high frequency arc, medium is medium frequency arc and low is low frequency arc.

Table 3. Chemical capacitance of the five nickelates at a temperature of 600°C.

Table 1.

Temperature	x = 0.00	x = 0.05	x = 0.15	x = 0.25	x = 0.35
600°C	54.4 Ωcm^2	24.9 Ωcm^2	24.8 Ωcm^2	23.8 Ωcm^2	63.4 Ωcm^2
700°C	7.19 Ωcm^2	3.19 Ωcm^2	3.69 Ωcm^2	3.89 Ωcm^2	9.51 Ωcm^2
800°C	1.78 Ωcm^2	0.65 Ωcm^2	0.89 Ωcm^2	1.15 Ωcm^2	2.51 Ωcm^2

Table 2.

	High		Medium		Low	
Compound	ASR	n	ASR	n	ASR	n
x = 0.00	3.76 Ωcm^2	0.77	33.0 Ωcm^2	0.24	17.6 Ωcm^2	0.72
x = 0.05	6.53 Ωcm^2	0.80	6.97 Ωcm^2	0.39	11.4 Ωcm^2	0.70
x = 0.15	7.53 Ωcm^2	0.91	5.33 Ωcm^2	0.81	11.9 Ωcm^2	0.42
x = 0.25	3.42 Ωcm^2	0.81	-	-	20.4 Ωcm^2	0.50
x = 0.35	9.74 Ωcm^2	0.84	32.5 Ωcm^2	0.49	21.0 Ωcm^2	0.64

Table 3.

compound	x = 0.00	x = 0.05	x = 0.15	x = 0.25	x = 0.35
C_{chem}	5.34 $mFcm^{-2}$	130 $mFcm^{-2}$	18.0 $mFcm^{-2}$	1.02 $mFcm^{-2}$	43.0 $mFcm^{-2}$

Figure captions:

Figure 1. EIS spectrum of a $La_{1.95}Sr_{0.05}NiO_4$ cone-shaped electrode measured in air at 600^oC. Circles are measured data. Solid line is fitted data. The EIS data were fitted with the circuit $R_s(R_1Q_1)(R_2Q_2)(R_3Q_3)$.

Figure 2. The variation of the total ASR with x at 600^oC in air.
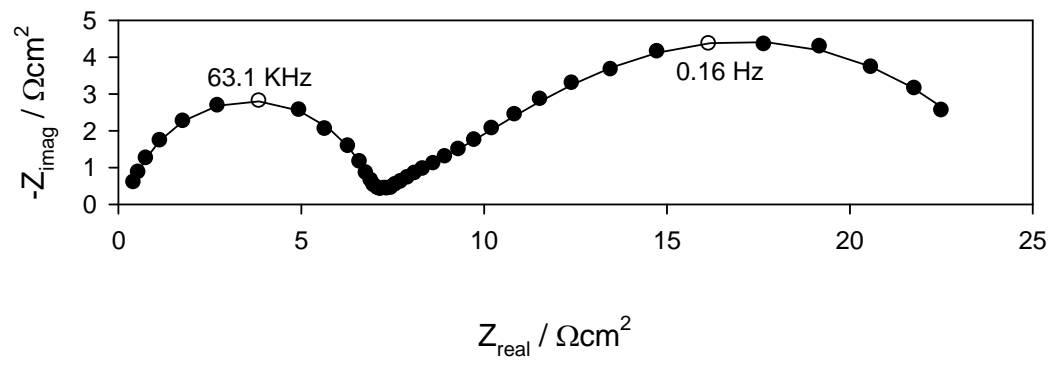
Figure 1.

Figure 2.