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Letter

Cone-Shaped $\text{Gd}_{1-x}\text{Sr}_x\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ Electrodes for SOFC Cathodes

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Five $\text{Gd}_{1-x}\text{Sr}_x\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ perovskites were synthesized using the glycine-nitrate process. The compounds were evaluated as solid oxide fuel cell cathodes using cone-shaped electrodes and electrochemical impedance spectroscopy. It was shown that the electrochemical activity depended on the amount of strontium in the perovskite; the main difference seemed to be whether the perovskite is a single or a two-phase compound. However, high-strontium-substituted Fe-Co-based perovskites have slightly higher performances than the low-strontium-substituted Fe-Co-based perovskites, as determined by electrochemical impedance spectroscopy on cone-shaped electrodes.

Keywords: SOFC; Cathode; Perovskite; Cone-shaped electrodes; EIS

1. INTRODUCTION

The solid oxide fuel cell (SOFC) is an electrochemical device for the direct conversion of chemical energy into electricity and heat [1]. One major obstacle in commercializing the SOFC is achieving a decrease in the operation temperature of the fuel cell [2]. To achieve this, new cathode materials must be developed instead of the commonly used $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3+\delta}$ (LSMx)-based cathodes. It has previously been shown that the performance of the perovskite $\text{Gd}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ is outstanding, probably due to the formation of two perovskite phases with a unique micro-structure [3, 4]. However, $\text{Gd}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ reacts with zirconia-based electrolytes, probably forming SrZrO_3 as a reaction product [5]. Only a very few studies of Gd-based Fe-Co perovskites as SOFC cathodes has been reported in the literature [6,7]. In this study, the amount of strontium is varied, and the electrochemical performance is evaluated using cone-shaped electrodes and electrochemical impedance spectroscopy (EIS) to evaluate the effect of the amount of strontium on the performance of

this type of perovskite in SOFC cathodes. Powder XRD is used to reveal the phases present in the powders. Newman's formula is used to find the contact areas of the cone-shaped electrodes [8]. Newman's formula is given below:

$$(1) r = 1/4R_s\sigma^*,$$

where R_s is the intercept at high frequency with the real axis in the impedance plot, and σ^* is the specific conductivity of the electrolyte. An electrolyte conductivity of 0.0167 S/cm at 600 °C is used throughout 600°C [9],[7]. Additionally, r is the radius of the contact point between the electrode and the electrolyte.

2. EXPERIMENTAL

Powders of the perovskites were made using the glycine-nitrate process described in detail elsewhere [10]. In general, the powders were made by mixing metal-nitrate solutions in the appropriate ratio in a beaker. Glycine was then added, and the solution was heated on a hot plate until ignition. The resulting powder was transferred to a crucible and heat treated at 1100 °C for 12 h. Cylinders of the powders were made by pressing the powder in an appropriate die. The cylinders were sintered at 1250 °C for 12 h before being machined into cones using diamond tools. The cones were tested by pushing them vertically against a CGO10 ($\text{Ce}_{1.9}\text{Gd}_{0.1}\text{O}_{1.95}$) electrolyte. A weight of approximately 100 g was used throughout. As a counter/reference electrode, a silver electrode was used. The cathodes were evaluated using a Solartron 1260 phase-gain analyzer. Five points were recorded at each decade in the frequency range 1 MHz to 0.05 Hz. A 25 mV amplitude was used throughout. The EIS measurements were recorded at the temperatures 800, 700 and 600 °C (in the given order). An equilibration time of 24 h at temperature was used before the measurements. The EIS data were treated using the PC-Windows program 'equivcrt' by *Boukamp* [11]. As few RQ components as possible were used in the fitting. Q is a constant phase element with the admittance:

$$(2) Y = Y_0(j\omega/\omega_0)^n,$$

where Y_0 is a constant, ω is the cyclic frequency, and n is an exponent. Y_0 and n are found from the fitting. In general, 2 to 4 RQs were used in the fitting.

3. RESULTS

Powder XRD reveals that the compounds with x equal to 0.1, 0.4 and 0.5 are of dual phases and that they belong to the cubic and the orthorhombic crystal systems. The compounds with x equal

to 0.2 and 0.3 are single-phase perovskites belonging to the orthorhombic crystal system. The unit cell parameters for the five compounds can be found in Table 1. The results from the EIS study can be found in Table 2 in the form of the total area specific resistance (ASR). An example of an electrochemical impedance spectrum can be found in Figure 1, together with the fitting result. The total ASR values as a function of x at 600 °C can be found in Figure 2.

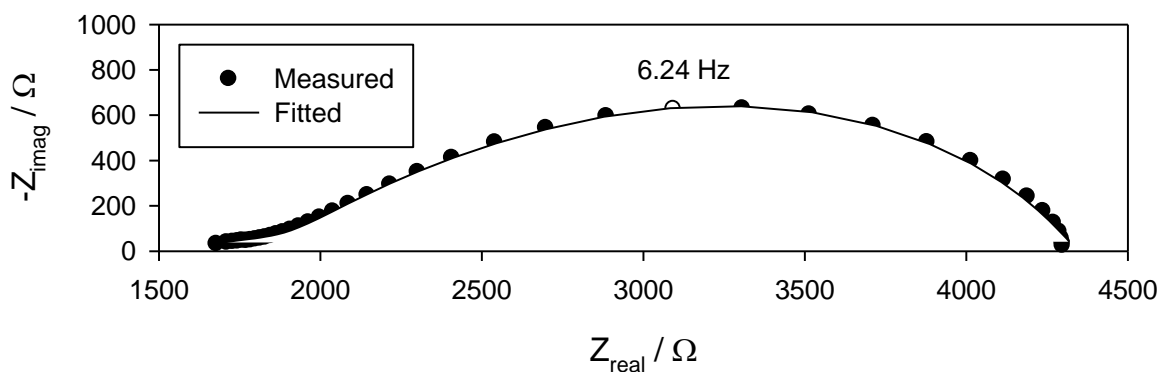


Figure 1. Measured and fitted EIS spectrum measured on a cone-shaped electrode with the composition $Gd_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ in air at 600 °C.

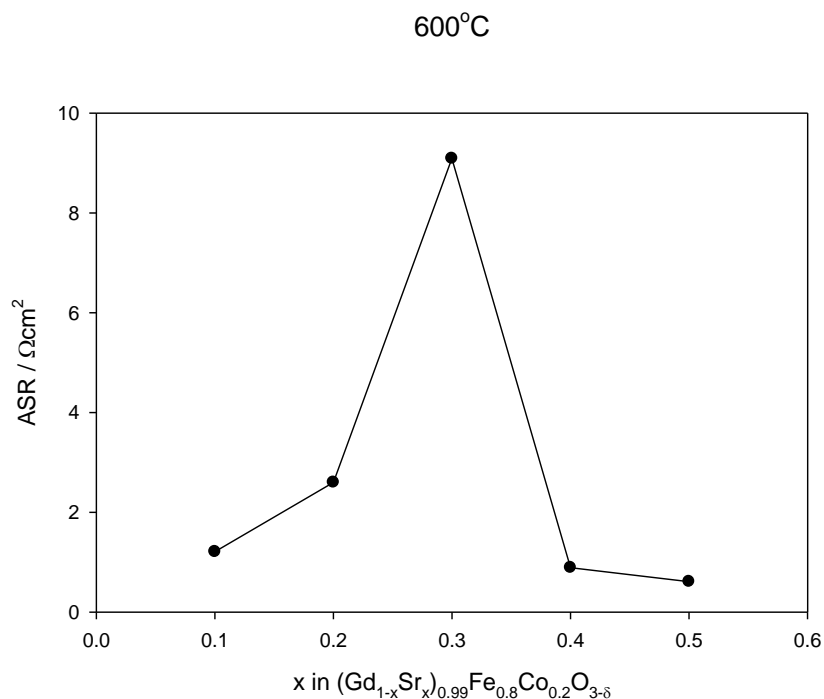


Figure 2. The total ASR values as a function of x in $Gd_{1-x}Sr_xFe_{0.8}Co_{0.2}O_{3-\delta}$ at 600 °C in air.

Table 1. Unit cell parameters of $Gd_{1-x}Sr_xFe_{0.8}Co_{0.2}O_{3-\delta}$ perovskites measured by powder XRD at room temperature in air.

	0.1	0.2	0.3	0.4	0.5
A	7.6636(17)	7.6588(17)	7.6436(20)	7.6243	7.6613
B	5.5882(12)	5.5812(13)	5.5766(17)	5.5572	5.5611
C	5.3494(15)	5.3475(12)	5.3454(14)	5.3276	5.3324
A'	3.8376(16)			3.8270	3.8325

Table 2. Total ASR values for $Gd_{1-x}Sr_xFe_{0.8}Co_{0.2}O_{3-\delta}$ perovskites measured at three different temperatures in air using EIS.

Material/temp.	x = 0.1	x = 0.2	x = 0.3	x = 0.4	x = 0.5
600 °C	1.14 Ωcm^2	2.46 Ωcm^2	9.04 Ωcm^2	0.77 Ωcm^2	0.65 Ωcm^2
700 °C	0.19 Ωcm^2	0.36 Ωcm^2	1.49 Ωcm^2	0.13 Ωcm^2	0.14 Ωcm^2
800 °C	0.06 Ωcm^2	0.12 Ωcm^2	0.25 Ωcm^2	0.04 Ωcm^2	0.05 Ωcm^2

Table 3. ASR of the individual arcs measured at 600 °C in air. R_1 is the high-frequency arc and so on.

x	0.1		0.2		0.3		0.4		0.5	
Arc	ASR	n	ASR	n	ASR	N	ASR	n	ASR	n
$R_1 / \Omega\text{cm}^2$	0.01	1.00	0.003	1.00	0.003	1.00	-	-	0.09	0.90
$R_2 / \Omega\text{cm}^2$	0.01	0.34	0.01	0.52	-	-	0.11	0.29	-	-
$R_3 / \Omega\text{cm}^2$	0.65	0.48	0.50	0.50	1.58	0.48	0.24	0.57	0.56	0.48
$R_4 / \Omega\text{cm}^2$	0.47	0.77	1.95	0.77	7.46	0.82	0.42	0.72	-	-

As can be seen the amount of Sr has an influence on the performance of the cathodes, as a factor of more than 10 difference in ASR values is observed between the single- and the dual-phase compounds. In Table 3, the ASR values of the individual arcs are given at a temperature of 600 °C. The largest difference is observed for the low-frequency arc.

4. DISCUSSION

Jørgensen and Mogensen [12] and Siebert et al. [13] have suggested a mechanism that can be used to interpret EIS data. In the mechanism suggested by Siebert et al., the high-frequency arc is due to the transfer of oxide anions (O^-) at the electrode/electrolyte interface. Calculation of the equivalent capacity for this arc can be done with the equation given below [14]:

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

The calculated capacitances for this arc are in the range of the double layer capacitance [15]. The two medium-frequency arcs can be attributed to diffusion processes, either in the bulk of the electrode material or on the surface of the electrode [12]. The low-medium-frequency arc has an n value close to 0.5, as expected for a Warburg diffusion process. The low-frequency arc is normally attributed to a slow oxygen-exchange reaction at the electrode surface [12, 13]. 10, 11]. This arc magnitude changes the most with the electrode material composition. This indicates that bond breaking occurs most rapidly in the strontium-rich compounds. It also indicates that bond breaking occurs more rapidly in the two-phase compounds than in the one-phase compounds. This could be due to the small particles of one of the phases (the cubic phase) [4]. The equivalent capacities calculated for the low-frequency arc are in the range depicted for chemical capacitance [15].

5. CONCLUSION

The amount of strontium has an influence on the electrochemical performance of $Gd_{1-x}Sr_xFe_{0.8}Co_{0.2}O_{3-\delta}$ compounds. However, high-strontium-substituted Fe-Co-based perovskites have only a slightly higher electrochemical performance than low-strontium-substituted Fe-Co-based perovskites, as determined by EIS. This opens the possibility of decreasing the reactivity of Fe-Co-based perovskites toward zirconia-based electrolytes by lowering the amount of strontium in the perovskite structure. It also seems that two-phase compounds perform better than single-phase compounds.

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