Article

Impact of Silica Additions on the Phase Composition and Electrical Transport Properties of Ruddlesden-Popper $\text{La}_2\text{NiO}_{4+\delta}$ Mixed Conducting Ceramics

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Abstract: The present work explores the possibility of incorporation of silicon into the crystal structure of Ruddlesden-Popper $\text{La}_2\text{NiO}_{4+\delta}$ mixed conducting ceramics with the aim to improve the chemical compatibility with lanthanum silicate-based solid electrolytes. Ceramics with the nominal composition $\text{La}_2\text{Ni}_{1-y}\text{Si}_y\text{O}_{4+\delta}$ ($y = 0, 0.02$ and 0.05) were prepared by the glycine nitrate combustion technique and sintered at 1450°C . While minor changes in the lattice parameters of the tetragonal K_2NiF_4 -type lattice may suggest incorporation of a small fraction of Si into the Ni sublattice, combined XRD and SEM/EDS studies indicate that this fraction is very limited ($\ll 2$ at.%, if any). Instead, additions of silica result in segregation of apatite-type $\text{La}_{10-x}\text{Si}_6\text{O}_{26+\delta}$ and La_2O_3 secondary phases as confirmed experimentally and supported by the static lattice simulations. Both total electrical conductivity and oxygen-ionic transport in $\text{La}_2\text{NiO}_{4+\delta}$ ceramics are suppressed by silica additions. The preferential reactivity of silica with lanthanum oxide opens a possibility to improve the compatibility between lanthanum silicate-based solid electrolytes and $\text{La}_2\text{NiO}_{4+\delta}$ -based electrodes by appropriate surface modifications. The promising potential of this approach is supported by preliminary tests of electrodes infiltrated with lanthanum oxide.

Keywords: solid oxide fuel cell; solid electrolyte; apatite; lanthanum silicate; Ruddlesden-Popper phase; lanthanum nickelate; electrical conductivity; oxygen permeability; electrode polarization

Citation: Zakharchuk, K.; Bamburov, A.; Naumovich, E.N.; Vieira, M.A.; Yaremchenko, A.A. Impact of Silica Additions on the Phase Composition and Electrical Transport Properties of Ruddlesden-Popper $\text{La}_2\text{NiO}_{4+\delta}$ Mixed Conducting Ceramics. *Processes* **2022**, *10*, 82. <https://doi.org/10.3390/pr10010082>

Academic Editor: Lucía dos Santos-Gómez

Received: 2 December 2021

Accepted: 28 December 2021

Published: 31 December 2021

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1. Introduction

Solid oxide fuel cells (SOFCs) are one of the most promising technologies for future power generation with expected gains in efficiency compared to conventional combustion-based technologies and with a wide range of potential applications including power sources for remote areas, transportation, and small to large-scale stationary power applications [1–3]. In addition to high energy conversion efficiency, the advantages of SOFC technology include fuel flexibility (from hydrogen to natural gas and biogas), low emissions and noiseless operation. The research in the SOFC area in recent years has been focused on lowering the operating temperature to $500\text{--}800^\circ\text{C}$, thus aiming to reduce the system cost and improve cell durability [3].

Rare-earth silicates with apatite-type structure have attracted significant attention in the last two decades as a promising group of comparatively low-cost materials for use as solid electrolytes in the intermediate-temperature SOFCs [4–9]. The compounds have the general formula $\text{M}_{10}(\text{SiO}_4)_6\text{O}_{2+z}$, where M is a rare-earth or alkaline-earth metal.

Lanthanum silicates exhibit the highest conductivities and show nearly pure oxygen-ionic conductivities over a wide range of oxygen partial pressures [10–14]. A number of studies of chemical substitutions aimed at optimizing the ionic conductivity showed that silicate apatites can tolerate a wide range of dopants and that the conductivity depends on the degree of anion or cation nonstoichiometry. The level of oxygen-ionic transport in lanthanum silicates with optimized composition is higher than in state-of-the-art yttria-stabilized zirconia electrolytes below 800 °C and achieves values > 0.001 S/cm at 500 °C being comparable with the highest conductivity reported for other solid electrolytes such as doped ceria and lanthanum gallate [8–12].

Despite substantial interest in apatite-type solid electrolytes, there have been a rather limited number of reports on the behavior of electrode materials in contact with these silicates [7,15–27]. Analysis of the available literature indicates that it is the chemical incompatibility between cell components and insufficient electrochemical performance of electrodes in contact with silicate-based solid electrolytes that may hinder their implementation in the SOFC technology. Typically, no formation of insulating phases between the lanthanum silicate-based electrolyte and the electrode materials was detected even at temperatures above 1100 °C [7,19–25]. However, noticeable cation interdiffusion between the electrolyte and electrode at the interface and silica diffusion from the electrolyte surface is often observed [7,15,16,22–25]. These factors may result in the deterioration of transport properties at the interfacial layers of both electrode and electrolyte and partial blocking of the electrochemical reaction zone, and, therefore, seem to be responsible for the rather poor behavior of tested cathode and anode materials. This is verified by the observation that polarization resistance increases with electrode fabrication temperature [7,24]. Among tested cathode materials, perovskite-type manganites showed the worst performance [7,15,16,21–23] due to significant cation interdiffusion and low ionic conductivity at the intermediate temperatures. Although attractive results were reported for perovskite-related Ruddlesden-Popper $\text{Ln}_2\text{NiO}_{4+\delta}$ -based nickelates, overpotential values are still high at temperatures below 800 °C [19,22,23,26].

Rare-earth nickelates $\text{Ln}_2\text{NiO}_{4+\delta}$ belong to the family of layered Ruddlesden-Popper (RP) phases with the general formula $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$. The RP-type structure of Ln_2NiO_4 with $n = 1$, or K_2NiF_4 -type structure, is built of perovskite-type LnNiO_3 layers alternating with rock-salt-type LnO layers along the crystallographic c axis. A characteristic feature of $\text{Ln}_2\text{NiO}_{4+\delta}$ nickelates is their ability to accommodate excess oxygen that is incorporated in the interstitial positions in the rock-salt-type layers and is responsible for oxygen-ionic transport in these phases [28–31]. Substantial electronic conductivity (~ 50 – 100 S/cm at 500–800 °C) and high oxygen diffusion coefficients ensure the competitive electrochemical performance of mixed-conducting $\text{Ln}_2\text{NiO}_{4+\delta}$ -based oxygen electrodes in SOFCs [28–32].

As the Ln_2NiO_4 structure is very flexible to different kinds of substitutions in both sublattice, one possible approach to improve the compatibility of Ln_2NiO_4 -based electrodes with apatite-type lanthanum silicate solid electrolytes may be the incorporation of silicon cations into the Ln_2NiO_4 lattice aiming to reduce the chemical potential gradient of silicon and therefore the driving force for unfavorable silica diffusion. The substitutions by silicon into perovskite-related oxides for electrochemical applications are not common but generally can be implemented [33]. In particular, the possibility of partial substitution of B-site transition metal cations by silicon and the formation of solid solutions were reported for $\text{SrM}_{1-y}\text{Si}_y\text{O}_{3-\delta}$ ($M = \text{Co}, \text{Fe}, \text{Mn}$) [34–36], $\text{Sr}_{1-x}\text{Ca}_x\text{M}_{1-y}\text{Si}_y\text{O}_{3-\delta}$ ($M = \text{Mn}, \text{Fe}$) [37,38], $\text{A}_2\text{MnFe}_{1-y}\text{Si}_y\text{O}_{6-\delta}$ ($A = \text{Ca}, \text{Sr}$) [39], $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{1-y-z}\text{Fe}_y\text{Si}_z\text{O}_{3-\delta}$ [40] and $\text{Sr}_{0.9}\text{Y}_{0.1}\text{Co}_{1-y}\text{Si}_y\text{O}_{3-\delta}$ [40] systems, often with positive effects on structural properties and electrical conductivity.

Thus, the goal of this work was to explore the possibility of incorporation of silicon cations into the nickel sublattice of $\text{La}_2\text{NiO}_{4+\delta}$ and to evaluate the impact of silica additions on the electrical transport properties. The phase formation was analyzed by X-ray diffraction combined with microstructural studies and static lattice simulations. The characterization included the measurements of electrical conductivity and oxygen permeability

and preliminary assessment of the electrochemical performance of $\text{La}_2\text{NiO}_{4+\delta}$ -based electrodes in contact with apatite-type lanthanum silicate-based electrolytes by electrochemical impedance spectroscopy.

2. Materials and Methods

The powders with the nominal composition $\text{La}_2\text{Ni}_{1-y}\text{Si}_y\text{O}_{4+\delta}$ ($y = 0, 0.02$ and 0.05) were synthesized by the glycine-nitrate combustion technique using $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Sigma-Aldrich, St. Louis, Mo, USA), Ni (99.7%, Sigma-Aldrich), SiO_2 (extra pure, Merck) and glycine ($\geq 99\%$, Sigma Aldrich) as the starting chemical. Ni was dissolved in a minimum amount of nitric acid to yield nickel nitrate. The calculated amount of highly dispersed silica was added to the aqueous solution containing appropriate amounts of lanthanum and nickel nitrates and glycine (glycine/nitrate molar ratio was double with respect to stoichiometric reaction). After stirring for several hours, the homogeneous suspension was heated on a hot plate until evaporation of water and auto-ignition. The foam-like combustion products were fired 3 times at $950^\circ\text{C}/5\text{ h}$ with intermediate regrinding to burn out organic residues and attain phase homogeneity. The as-synthesized powders were ball milled with ethanol (Retsch S1 mill, nylon vial, tetragonal zirconia balls) for 4 h at 150 rpm. After drying, the samples with $x = 0.05$ were subjected to heat treatments in the powdered or pelletized form to evaluate possible changes in the phase composition with temperature. Final ceramic samples of all materials were compacted uniaxially in a disk-shaped form and sintered at 1450°C for 5 h.

The density of prepared ceramics (ρ_{exp}) was calculated from the geometric dimensions and mass of polished samples. Rectangular bars ($\sim 1.5 \times 2.5 \times 12\text{ mm}$) for electrical measurements were cut out of disk-shaped samples. Powdered samples for X-ray diffraction (XRD) were prepared by grinding sintered ceramics in a mortar. XRD data were recorded on a Rigaku D/Max-B diffractometer (CuK_α radiation). The unit cell parameters were calculated in FullProf software (profile matching method). Microstructural characterization was conducted by scanning electron microscopy (SEM) using a Hitachi SU-70 microscope equipped with Bruker Quantax 400 detector for energy dispersive spectroscopy (EDS) analysis.

Electrical conductivity (σ) was measured as a function of temperature and oxygen partial pressure $p(\text{O}_2)$ by the four-probe DC technique using bar-shaped samples. Pt wires were used as probes and current collectors. The end-face surfaces of the bars were covered with Pt paint (Heraeus CL11-5349) to improve the electrical contact. The oxygen partial pressure was imposed by the composition of flowing $\text{N}_2 + \text{O}_2$ gas mixtures set using Bronkhorst mass-flow controllers. The values of $p(\text{O}_2)$ were monitored employing a home-made potentiometric yttria-stabilized zirconia (YSZ) sensor. The measurements of oxygen permeation fluxes through dense ceramic membranes were performed at $750\text{--}950^\circ\text{C}$ using electrochemical YSZ solid electrolyte cells comprising an oxygen pump and a sensor [41,42]. The oxygen partial pressure at the membrane feed side (p_2) was equal to 0.21 atm (atmospheric air). The thickness of the disk-shaped membranes (d) was 1.00 mm. The gas tightness of the samples before the measurements was verified by the absence of physical leakages under the total pressure gradient of 2–3 atm at room temperature.

The electrochemical characterization of $\text{La}_2\text{NiO}_{4+\delta}$ -based electrodes in contact with a $\text{La}_{3.83}\text{Pr}_6\text{Si}_{4.5}\text{Fe}_{1.5}\text{O}_{26}$ solid electrolyte was performed using electrochemical cells with a symmetrical electrode | electrolyte | electrode configuration. The electrolyte material was synthesized as described in [43]. Dense disk-shaped solid electrolyte membranes with a theoretical density of $\sim 96\%$ were sintered at 1650°C for 15 h. The electrode ink was prepared by adding as-synthesized $\text{La}_2\text{NiO}_{4+\delta}$ powder (30 vol.%) to a solution containing a binder (ethyl cellulose, 5 wt.%) and a dispersant (stearic acid, 3 wt.%) in α -terpineol and ball-milling for several hours. Porous $\text{La}_2\text{NiO}_{4+\delta}$ electrode layers (diameter 5 mm) were painted symmetrically on both sides of polished electrolyte pellets and sintered at 1300°C for 2 h. The electrochemical activity of electrodes was evaluated by electrochemical impedance spectroscopy (EIS) using an AUTOLAB PGSTAT 302 potentiostat/galvanostat with a built-in FRA module (AC amplitude 50 mV, frequency range 10 mHz–1 MHz).

The surface modification of electrode layers was performed by infiltration of an aqueous solution of lanthanum nitrate into the porous electrode structure followed by calcination at 1000 °C for 2 h.

The simulations of the $\text{La}_2\text{NiO}_{4+\delta}$ lattice were performed in atomistic software using phenomenological potentials. GULP code [44,45] was used for geometry optimization and the evaluation of the lattice energy. In order to obtain the lattice energy of apatite-type silicate lattice, a preliminary generated supercell was treated employing Monte-Carlo simulations in DL_MONTE2 software [46,47] to reach reasonable distribution of ions between partially populated sites in the lanthanum and oxygen sublattices. The most stable configuration obtained in the Monte-Carlo run was selected for the structure optimization in GULP. GULP and DL_MONTE share compatible sets of interatomic potentials that describe interactions of ions with formal charges in the crystalline lattice including the electrostatic term:

$$U_{ij}^{\text{Coulomb}} = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}, \quad (1)$$

where r_{ij} is the distance between ions with the charges q_i and q_j , and the Buckingham term:

$$U_{ij}^{\text{Buckh}} = A \exp\left(-\frac{r_{ij}}{\rho}\right) - \frac{C_6}{r_{ij}^6}, \quad (2)$$

where A , ρ and C_6 are the constants characteristic for each pair of ions. An additional three-body potential was employed for the $\text{O}^{2-}\text{-Si}^{4+}\text{-O}^{2-}$ bonds:

$$U_{ij}^{3b} = \frac{1}{2} k_{3b} (\theta - \theta_0)^2, \quad (3)$$

where k_{3b} is the angle spring constant, θ_0 is the characteristic angle for a given triplet, and θ is the actual angle. The core-shell model was used to account for the polarizability of La^{3+} and O^{2-} cations:

$$E_i^{\text{pol}} = \frac{1}{2} k_{sp} r^2, \quad (4)$$

where r is the shift of the shell relative to the core and k_{sp} is the spring constant. The parameters of phenomenological potentials were collected from the published data and are listed in Table 1. The potential cut-off during the simulations was 18 Å for GULP and 12 Å for DL_MONTE2.

Table 1. Interatomic potentials used for the lattice simulation.

Interaction	Buckingham Term			Core-Shell Term		Three-Body Term		Ref.
	A , eV	ρ , Å	C , Å ⁻⁶	γ , e	k_{sp} , eV Å ⁻²	k_{3b} , eV rad ⁻²	θ_0 , °	
$\text{O}^{2-}\text{-O}^{2-}$	22,764.3	0.149	27.89	−2.860	74.92			[48]
$\text{La}^{3+}\text{-O}^{2-}$	4579.23	0.30437	-	−0.250	145.00			[48]
$\text{Ni}^{2+}\text{-O}^{2-}$	1582.50	0.28820	-	-	-			[49]
$\text{Si}^{4+}\text{-O}^{2-}$	1283.91	0.32052	10.66	-	-			[48]
$\text{O}^{2-}\text{-Si}^{4+}\text{-O}^{2-}$						2.097240	109.47	[50]

3. Results

XRD analysis of the $y = 0.05$ powder after firing at 1100 °C (three times for 5 h with intermediate regrinding) revealed the presence of phase impurities in addition to the main tetragonal K_2NiF_4 -type phase (Figure 1A). Taking into account the results of SEM/EDS analysis (discussed below), most extra reflections were assigned to an apatite-type $\text{La}_{10-x}\text{Si}_6\text{O}_{26+\delta}$ silicate phase. This phase could not be eliminated by increasing the temperature of thermal treatment to 1350–1450 °C and its fraction remained virtually unchanged (Figure 1B–D). Tiny additional impurity peaks on the background level coincide

with the positions of the main reflections of La_2O_3 . (Figure 1A). The presence of this phase impurity was detectable only in selected XRD patterns.

Figure 1. XRD patterns of $\text{La}_2\text{Ni}_{0.95}\text{Si}_{0.05}\text{O}_{4+\delta}$ samples after thermal treatments: (A) powder and (B–D) compacted samples sintered at different temperatures.

The final ceramic samples of all compositions were sintered at 1450 °C for 5 h. The parent silicon-free nickelate was phase pure. The other two compositions contained $\text{La}_{10-x}\text{Si}_6\text{O}_{26+\delta}$ impurity and, apparently, trace amounts of La_2O_3 (Figure 2). The fraction of lanthanum silicate phase increased with increasing the nominal silicon content.

The XRD patterns of all compositions were indexed in the tetragonal $I4/mmm$ space group. Additions of silicon have only a minor effect on the lattice parameters of the tetragonal K_2NiF_4 -type lattice (Table 2). Still, the addition of silica results in a slight shrinkage in the basal a - b plane and a modest elongation along the c -axis. This could be explained by the incorporation of higher-valence small Si^{4+} cations ($r^{\text{VI}}(\text{Si}) = 0.40 \text{ \AA}$ [51]) into the Ni sublattice ($r^{\text{VI}}(\text{Ni}^{2+}) = 0.69 \text{ \AA}$ [51]), with expansion along the c -axis caused by incorporation of extra interstitial oxygen required to maintain the electroneutrality condition.

Similar to the parent $\text{La}_2\text{NiO}_{4+\delta}$ ceramics, the $y = 0.02$ samples were gas-tight with comparatively low porosity (Figure 3A) and a relative density of 95% of the theoretical (Table 2). Increasing silica additions resulted in noticeably worse sinterability under identical conditions. The ceramics with the nominal composition $\text{La}_2\text{Ni}_{0.95}\text{Si}_{0.05}\text{O}_{4+\delta}$ had a substantial porosity (Figure 3C) and a relative density of only ~80%. Apart from the pores, the microstructural studies revealed the presence of well-distributed inclusions (appearing with a darker contrast in the SEM images) in both silicon-containing materials (Figure 3). The size of inclusions and their concentration were found to increase with increasing silica additions.

Figure 2. XRD patterns of $\text{La}_2\text{Ni}_{1-y}\text{Si}_y\text{O}_{4+\delta}$ ceramics sintered at 1450 °C for 5 h.

Table 2. Lattice parameters and density of $\text{La}_2\text{Ni}_{1-y}\text{Si}_y\text{O}_{4+\delta}$ ceramics sintered at 1450 °C.

Composition	Unit Cell Parameters			Density ρ_{exp} , g/cm ³	Relative Density $\rho_{\text{exp}}/\rho_{\text{theor}}$, % ¹
	a , Å	c , Å	V , Å ³		
0	3.8636(1)	12.6662(2)	189.07(1)	6.82	96.3
0.02	3.8611(1)	12.6784(4)	189.02(1)	6.73	95.2
0.05	3.8610(1)	12.6831(4)	189.08(1)	5.60	79.5

¹ ρ_{theor} was estimated from the structural data assuming nominal composition with $\delta = 0.15$ and neglecting phase impurities.

Despite the visual similarities, SEM/EDS inspections showed that there are two types of inclusions. One example is shown in Figure 4. The distribution of lanthanum seemed to be comparatively homogeneous. The inclusions of the first type are enriched with silicon and depleted with nickel. These are the most frequent inclusions corresponding to the $\text{La}_{2-x}\text{Si}_6\text{O}_{26+\delta}$ impurity phase. More rare inclusions (spot 2 in Figure 4) are depleted in both nickel and silicon and were assigned to La_2O_3 impurity.

Thus, the results of XRD and SEM/EDS studies imply that the solubility of silicon in the nickel sublattice of $\text{La}_2\text{NiO}_{4+\delta}$ is extremely limited under applied synthesis conditions. It is much less than 2 at.% and tends to zero. Instead, silica reacts with lanthanum oxide during the synthesis to yield an apatite-type lanthanum silicate phase. Trace amounts of lanthanum oxide segregate, apparently, to compensate for La:Si < 2 ratio in the apatite-type phase.

Figure 3. SEM images of polished $\text{La}_2\text{Ni}_{1-y}\text{Si}_y\text{O}_{4+\delta}$ ceramics.

Figure 4. SEM image of the polished surface of $\text{La}_2\text{Ni}_{0.98}\text{Si}_{0.02}\text{O}_{4+\delta}$ ceramics and corresponding EDS elemental maps. Spots 1 and 2 correspond to $\text{La}_{2-x}\text{Si}_6\text{O}_{26+\delta}$ and La_2O_3 impurity phase inclusions, respectively.

As the phase composition of oxide materials can be strongly influenced by the synthetic route, the possibility of the formation of a La_2NiO_4 -based solid solution containing silicon ions in the nickel sublattice was assessed by the static lattice simulations. $\text{La}_2^{3+}\text{Ni}^{2+}\text{O}_4^{2-}$ was considered as a host lattice, with all nickel in a 2^+ oxidation state. The simulated supercells, their dimensions and lattice energy are listed in Table 3. The latter is a value calculated in GULP as a sum of all energy terms for interatomic interactions for a given oxide. The simulated supercell of silicon-substituted lanthanum nickelate had the full formula $\text{La}_{72}\text{Ni}_{35}\text{SiO}_{145}$ which can be reduced to approximately $\text{La}_2\text{Ni}_{0.972}\text{Si}_{0.028}\text{O}_{4.028}$.

Table 3. Simulated supercells and calculated lattice energies per formula unit.

Cation Composition	Supercell	Lattice Energy, eV/f.u.	Formation Energy ΔE^f , eV/f.u.
La_2O_3	$1 \times 1 \times 1$	−129.92	
La_2NiO_4	$3 \times 3 \times 2$	−171.40	
$\text{La}_{9.33}\text{Si}_6\text{O}_{26}$	$3 \times 3 \times 3$	−1395.06	
$\text{La}_2\text{Ni}_{0.972}\text{Si}_{0.028}\text{O}_{4.028}$	$3 \times 3 \times 2$, config.(i)	−173.66 ¹	0.24
	$3 \times 3 \times 2$, config.(ii)	−173.64	0.26
	$3 \times 3 \times 2$, config.(iii)	−173.61	0.29

¹ Unstable configuration.

It is necessary to note that the replacement of a nickel cation by a silicon ion should be accompanied by the incorporation of three oxygen ions into the interstitial positions in the rock-salt-type layers of the Ruddlesden-Popper La_2NiO_4 structure. One oxygen ion is required to keep the lattice's electroneutrality and compensate for the excessive oxidation state of Si^{4+} with respect to the host Ni^{2+} matrix. Two other oxygen anions must be pushed out of the perovskite layer to maintain a tetrahedral oxygen environment strongly preferred by silicon. Thus, the existence of three interstitial oxygen anions in the $\text{La}_2\text{Ni}_{0.972}\text{Si}_{0.028}\text{O}_{4.028}$ supercell was assumed. Three configurations involving Si-centered tetrahedron and interstitial O^{2-} ions were tested to address the impact of interactions between charged point defects: (i) two O_i^{2-} placed near Si and one on a sufficient distance; (ii) only one O_i^{2-} placed near Si; and (iii) all O_i^{2-} anions placed on a sufficient distance from the silicon cation. Contrary to the second and third configurations, the first configuration was found to be unstable (as was indicated by the presence of negative lines in the simulated phonon spectrum). The configuration (iii) of the $\text{La}_2\text{Ni}_{0.972}\text{Si}_{0.028}\text{O}_{4.028}$ supercell after the geometry optimization is presented in Figure 5.

The energy of the formation of hypothetical $\text{La}_2\text{Ni}_{0.972}\text{Si}_{0.028}\text{O}_{4.028}$ was calculated as:

$$\Delta E^f = E(\text{La}_2\text{Ni}_{0.972}\text{Si}_{0.028}\text{O}_{4.028}) - \frac{1}{162}E(\text{La}_2\text{O}_3) - \frac{1}{216}E(\text{La}_{9.33}\text{Si}_6\text{O}_{26}) - \frac{35}{36}E(\text{La}_2\text{NiO}_4), \quad (5)$$

with the coefficients balanced to maintain the cation ratio. Independently of the tested $\text{Si} - \text{O}_i^{2-}$ configuration, the calculations yielded nearly identical positive values of the formation energy for silicon-substituted lanthanum nickelate (Table 3). This implies that the segregation of apatite-type silicate and lanthanum oxide is energetically more favorable compared to the formation of a solid solution, in agreement with the experimental results.

Inspection of polished and thermally etched ceramic samples by SEM revealed that additions of silica strongly suppress the grain growth during the sintering. In particular, it was found that grain size varied between 3.5 and 20 μm in undoped $\text{La}_2\text{NiO}_{4+\delta}$ and decreased down to 0.8–4.0 μm for the $y = 0.02$ samples prepared under identical conditions. This seems to imply that the silicon-rich phase impurities not only precipitate as individual grains, but also may segregate at the grain boundaries inhibiting the mobility of grain boundaries during the sintering process due to the solute drag effect or Zener effect [52]. This also explained the worse sinterability (higher porosity) of the $y = 0.05$ ceramics.

Figure 5. Simulated $\text{La}_2\text{Ni}_{0.972}\text{Si}_{0.028}\text{O}_{4.028}$ supercell with configuration (iii) after geometry optimization.

Figure 6 presents the data on the electrical conductivity of $\text{La}_2\text{Ni}_{1-y}\text{Si}_y\text{O}_{4+\delta}$ ceramics. All compositions exhibit a similar shape of $\sigma - T$ curves in air (Figure 6A). Electrical conductivity is temperature activated in the low-temperature range and shows a smooth transition to metallic-like behavior at temperatures above $\sim 400\text{--}600^\circ\text{C}$, in agreement with literature data on parent $\text{La}_2\text{NiO}_{4+\delta}$ [30,53,54]. Additions of silica result in a gradual decrease in electrical conductivity: from 87 S/cm for $y = 0$ to 68 S/cm for $y = 0.02$ and to 36 S/cm for $y = 0.05$ at 800°C . Note that $\text{La}_{10-x}\text{Si}_6\text{O}_{26+\delta}$ -based solid electrolytes demonstrate total electrical conductivity several orders of magnitude lower compared to $\text{La}_2\text{NiO}_{4+\delta}$. For instance, the total conductivity of $\text{La}_{10}\text{Si}_{5.5}\text{Al}_{0.5}\text{O}_{26+\delta}$, one of the apatite-type silicates with the highest conductivity, corresponds to 5×10^{-2} S/cm at 800°C [10]. Thus, additions of silica seem to play a rather passive role in terms of the mechanism of electrical transport: electrical conductivity decreases with an increasing fraction of poorly conducting inclusions (and possibly grain boundaries) and pores, as generally expected for different kinds of materials [55]. One should also note that the values of electrical conductivity of $\text{La}_2\text{Ni}_{0.98}\text{Si}_{0.02}\text{O}_{4+\delta}$ obtained in this work are comparable or even exceed the values often reported in the literature for undoped $\text{La}_2\text{NiO}_{4+\delta}$ (e.g., refs. [53,54]); most likely, this should be assigned to the differences in porosity and microstructure.

Reducing oxygen partial pressure results in a decrease in the electrical conductivity of $\text{La}_2\text{Ni}_{1-y}\text{Si}_y\text{O}_{4+\delta}$ ceramics (Figure 6B), in agreement with the literature data for undoped lanthanum nickelate [56,57]. This is associated with the reversible oxygen release from the K_2NiF_4 -type lattice accompanied by the reduction in nickel cations and, therefore, a decrease in the concentration of electronic charge carriers:

where $\text{Ni}_{\text{Ni}}^{\bullet}$ and $\text{Ni}_{\text{Ni}}^{\times}$ correspond to Ni^{3+} and Ni^{2+} , respectively, and $\text{Ni}_{\text{Ni}}^{\bullet}$ is equivalent to electron-hole.

Figure 6. Electrical conductivity of $\text{La}_2\text{Ni}_{1-y}\text{Si}_y\text{O}_{4+\delta}$ ceramics as a function of temperature in air (A) and as a function of oxygen partial pressure at 900 °C (B).

Figure 7 shows the data on oxygen permeability of $\text{La}_2\text{NiO}_{4+\delta}$ and $\text{La}_2\text{Ni}_{0.98}\text{Si}_{0.02}\text{O}_{4+\delta}$ ceramic membranes. These measurements could not be performed for the material with higher silica content since $\text{La}_2\text{Ni}_{0.95}\text{Si}_{0.05}\text{O}_{4+\delta}$ ceramics had excessive porosity and were not gas tight. Additions of silica to $\text{La}_2\text{NiO}_{4+\delta}$ were found to suppress oxygen ionic transport through ceramic membranes. Similar to the case of electrical conductivity, this can be partially attributed to the increasing fraction of the poorly conducting phase in the bulk of ceramics impeding the oxygen transport. However, the drop in oxygen permeability with additions of silica is accompanied by an increase in activation energy of the permeation process. This can possibly be caused by one of two following factors. Assuming partial incorporation of silicon into Ni sites, one may expect strong trapping of mobile ionic species (interstitial oxygen ions) near the Si^{4+} cations with effects on overall oxygen-ion mobility and activation energy of ionic transport. For instance, the substitution of iron with silicon was reported to suppress oxygen-ionic conductivity in perovskite-type $\text{SrFe}_{1-y}\text{Si}_y\text{O}_{4-\delta}$ solid solutions [36]; this was explained by anion site exclusion effects and oxygen vacancy trapping near SiO_4 tetrahedra [58]. However, since the solubility of silicon in $\text{La}_2\text{NiO}_{4+\delta}$ lattices is extremely limited (if any), the more probable reason for the drop in oxygen permeability is inhibition of surface exchange kinetics due to partial blocking of the surface by silica species. Increasing surface exchange limitations by silica impurities or silica poisoning were reported earlier for other mixed conducting ceramic membranes (e.g., refs. [59,60]).

Thus, the presence of silica is unfavorable for the surface processes involving oxygen and, therefore, may inhibit the electrochemical activity of mixed-conducting ceramic electrodes. This is in agreement with literature data suggesting that, even though $\text{Ln}_2\text{NiO}_{4+\delta}$ electrodes show good chemical compatibility with apatite-type silicate electrolytes [19,23,26], the deterioration of electrochemical activity of electrodes occurs due to the surface diffusion or spreading of silica from electrolyte to electrode resulting in a partial blocking of the electrochemical reaction zone [22–24,26]. However, since silicon is practically insoluble in the $\text{La}_2\text{NiO}_{4+\delta}$ lattice and the preferential reactivity pathway is the formation of the $\text{La}_{10-x}\text{Si}_6\text{O}_{26+\delta}$ -based phase, this opens the opportunity to minimize the negative effects of silica diffusion from the silicate solid electrolyte onto the surface of La_2NiO_4 -based electrodes by additions of extra lanthanum oxide to the electrode. As a result, the reactivity between lanthanum oxide and diffusing silica may result in the formation of solid electrolyte particles thus extending the triple-phase

boundary instead of blocking the electrode active surface. A similar approach was proposed earlier for silica scavenging in contaminated zirconia and ceria solid electrolytes [61,62].

Figure 7. (A) Dependence of oxygen permeation fluxes through $\text{La}_2\text{Ni}_{0.98}\text{Si}_{0.02}\text{O}_{4+\delta}$ ceramic membrane on oxygen partial pressure gradient at 750–950 °C; (B) comparison of oxygen permeation fluxes through $\text{La}_2\text{Ni}_{1-y}\text{Si}_y\text{O}_{4+\delta}$ membranes under fixed $p(\text{O}_2)$ gradient.

The preliminary tests seem to support the potential efficiency of such an approach. Figure 8 compares the electrochemical impedance spectra of $\text{La}_2\text{NiO}_{4+\delta}$ applied onto apatite-type $\text{La}_{3.83}\text{Pr}_6\text{Si}_{4.5}\text{Fe}_{1.5}\text{O}_{26}$ solid electrolyte before and after infiltration. The spectra can be roughly fitted using a simple equivalent circuit $(R_{\text{Ohm}})(R_{\text{HF}} \parallel \text{CPE}_{\text{HF}})(R_{\text{LF}} \parallel \text{CPE}_{\text{LF}})$ where R is resistance, CPE is the constant phase element, R_{Ohm} is the ohmic resistance of the cell, HF and LF indicate high-frequency and low-frequency contribution to the electrode process, and total electrode polarization resistance is the sum of $R_{\text{HF}} + R_{\text{LF}}$. Two electrode contributions were estimated to have relaxation frequencies of around 8–9 kHz and 100–300 Hz, respectively. Although these preliminary impedance spectroscopy data are not sufficient for reliable conclusions about the impact of surface modification on the different stages of the electrode process, it is evident that the infiltration of lanthanum oxide resulted in a drop in electrode polarization resistance by ~ 1.5 times at 800 °C. The impact was lower when the temperature was increased to 900 °C, possibly due to enhanced silica diffusion at a higher temperature. Nonetheless, these results support the potential suitability of the method. Further detailed studies are planned to explore the impact of surface modifications (thermal treatment procedure, infiltrated fraction) on the electrode performance, limiting stages of electrode process, and long-term stability.

Figure 8. Electrochemical impedance spectra of $\text{La}_2\text{NiO}_{4+\delta}$ electrode, as prepared and infiltrated with lanthanum oxide, in contact with apatite-type $\text{La}_{3.83}\text{Pr}_6\text{Si}_{4.5}\text{Fe}_{1.5}\text{O}_{26}$ solid electrolyte at 800 °C (A) and 900 °C (B). The spectra are corrected for ohmic contribution.

4. Conclusions

Ceramics with the nominal composition $\text{La}_2\text{Ni}_{1-y}\text{Si}_y\text{O}_{4+\delta}$ ($y = 0, 0.02$ and 0.05) were prepared by the glycine-nitrate combustion method and sintered at 1450 °C. Minor changes in the a and c parameters of tetragonal K_2NiF_4 -type lattice with increasing y suggest possible partial incorporation of silicon cations into the nickel sublattice. However, the results of combined XRD and SEM/EDS studies indicate that the solubility of silicon in the $\text{La}_2\text{NiO}_{4+\delta}$ lattice is very limited ($\ll 2$ at.% in Ni sublattice, if any). Instead, additions of silica to $\text{La}_2\text{NiO}_{4+\delta}$ induce the precipitation of apatite-type $\text{La}_{10-x}\text{Si}_6\text{O}_{26+\delta}$ phase and traces of La_2O_3 . The preferential formation of secondary phases in place of $\text{La}_2\text{Ni}_{1-y}\text{Si}_y\text{O}_{4+\delta}$ solid solutions is supported by the static lattice simulations. The segregation of phase impurities suppresses the grain growth and results in a gradual decline in electrical conductivity and oxygen permeability of $\text{La}_2\text{NiO}_{4+\delta}$ ceramics with the increasing silicon content. Practical insolubility of silicon in the lanthanum nickelate lattice and preferential formation of apatite-type lanthanum silicate phase suggest the possibility to inhibit the degradation of La_2NiO_4 -based electrodes in contact with $\text{La}_{10-x}\text{Si}_6\text{O}_{26+\delta}$ solid electrolytes by additions of extra La_2O_3 to capture diffusing silica. The prospects of such an approach are supported by preliminary tests and will be explored in further work.

Author Contributions: Conceptualization and methodology, A.A.Y.; static lattice simulations, E.N.N.; investigation, K.Z., A.B., M.A.V. and A.A.Y.; writing—original draft preparation, A.A.Y. and E.N.N.; writing—review and editing, K.Z., A.B., E.N.N., M.A.V. and A.A.Y.; funding acquisition, A.A.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the project CARBOSTEAM (POCI-01-0145-FEDER-032295) funded by FEDER through COMPETE2020—Programa Operacional Competitividade e Internacionalização (POCI) and by national funds through FCT/MCTES, and by the project CICECO—Aveiro Institute of Materials (UIDB/50011/2020 and UIDP/50011/2020) financed by national funds through the FCT/MCTES and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. PhD scholarship of K.Z. is funded by the FCT (grant SFRH/BD/138773/2018). PhD scholarship of A.B. is funded by the FCT (grant SFRH/BD/150704/2020).

Data Availability Statement: Data are contained within the article and/or available from the corresponding author upon reasonable request.

Conflicts of Interest: The authors declare no conflict of interest.

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