

Article

Development and Research of Different Perovskitic Electrocatalysts Synthesized via Co-Precipitation

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Abstract

Reversible solid oxide cells (ReSOCs) represent one of the most promising electrochemical technologies for sustainable energy conversion and storage, yet their large-scale deployment remains constrained by electrode materials capable of sustaining stable performance under alternating oxidizing and reducing conditions. Reversible solid oxide cells require electrode materials that combine phase stability, chemical compatibility, redox tolerance and a microstructure suitable for gas transport and surface reactions. However, the relationships among cation composition, thermal processing, phase formation and local chemical homogeneity remain insufficiently understood, particularly for compositionally complex perovskite-related oxides. In this work, this problem was addressed through a comparative physicochemical screening of three candidate electrode materials synthesized by a simple co-precipitation route: two co-doped lanthanum ferrites, (La_{0.8}Sr_{1.2})(Fe_{0.9}Co_{0.1})O_{6+δ} (LSFC) and (La_{0.8}Ca_{1.2})(Fe_{0.9}Co_{0.1})O_{6+δ} (LCFC), and one high-entropy praseodymium nickelate, Pr(Ba_{0.8}Ca_{0.2})(Fe_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2})₂O_{6+δ} (PBC-HEO). DTA–TG analysis was used to determine the thermal decomposition and crystallization ranges of the precipitated precursors. Phase evolution as a function of calcination temperature was investigated by X-ray diffraction, while Raman and FTIR spectroscopy were employed to examine the local metal–oxygen environment and structural disorder. Raman spectroscopy confirmed the formation of perovskite-type metal–oxygen frameworks in all samples and revealed distinct redistributions of spectral weight between apical/equatorial (or symmetry-related) BO₆ stretching sub-modes and bending/tilting modes, reflecting different local defect-chemical mechanisms associated with A-site doping (Sr vs. Ca) in the Ruddlesden–Popper ferrites and B-site multi-cation occupancy in the double-perovskite PBC-HEO. Bulk and local elemental compositions were assessed by ICP-MS and SEM-EDS, respectively, and SEM was used to compare particle morphology and porosity. SEM-EDS analysis showed that PBC-HEO developed the most open and interconnected microstructure among the investigated powders, although accompanied by residual compositional heterogeneity. This morphology may favor gas accessibility; however, its effective impact on electrocatalytic performance requires dedicated surface area, porosimetry, electrical, and electrochemical



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measurements. LSFC formed a single major Ruddlesden–Popper phase only after high-temperature calcination, whereas LCFC retained calcium-containing secondary phases. PBC-HEO developed a major perovskite-related phase at 700 °C, accompanied by minor Zn-rich segregation. Under the selected processing conditions, PBC-HEO retained the finest and most interconnected porous microstructure, although it also displayed the highest local compositional heterogeneity. These results demonstrate that cation selection and thermal history jointly control phase stability, local disorder and microstructure, providing a basis for the subsequent electrochemical evaluation and optimization of perovskite-related ReSOC electrode materials.

Keywords: perovskite oxides; reversible solid oxide cells; high-entropy oxides; lanthanum ferrite; electrocatalysts; Raman spectroscopy

1. Introduction

Reversible solid oxide cells (ReSOCs) are considered promising electrochemical devices for the efficient conversion and storage of energy within low-carbon energy systems [1,2]. Their ability to operate alternately in fuel-cell mode, converting chemical energy into electricity, and in electrolysis mode, producing hydrogen, syngas or other energy vectors, makes them particularly attractive for integrating intermittent renewable-energy sources with chemical-energy storage technologies [3–6]. In comparison with separate fuel-cell and electrolyzer systems, reversible operation may reduce plant complexity and improve overall resource utilization. However, the same electrodes must remain functional under substantially different gas compositions, oxygen chemical potentials and electrochemical polarization conditions.

The large-scale deployment of ReSOCs is therefore still limited by materials-related challenges, particularly those concerning electrode activity, electrical and ionic transport, redox tolerance, phase stability and long-term compatibility with the other cell components [7–9]. During repeated transitions between fuel-cell and electrolysis operation, the electrodes can experience marked changes in oxygen partial pressure, local atmosphere and electrochemical potential. These conditions may promote cation segregation, secondary-phase formation, surface poisoning, grain coarsening, microstructural degradation, chemical interaction with the electrolyte and loss of electrochemically active sites [10–14]. The development of chemically and structurally stable electrode materials is consequently one of the principal requirements for improving the durability and reliability of reversible solid oxide electrochemical devices.

Perovskite and perovskite-related oxides represent an important family of candidate electrode materials because of their compositional and crystallographic flexibility [15,16]. Cation substitutions can be introduced on both the A and B sublattices, allowing the electronic structure, average cation valence, oxygen non-stoichiometry, vacancy concentration, thermal expansion and mixed ionic–electronic conductivity to be modified over broad compositional ranges [17–20]. These properties are especially relevant for electrode processes governed by the combined effects of charge transfer, gas adsorption and dissociation, oxygen surface exchange and oxygen-ion transport through the solid phase [21,22]. Layered Ruddlesden–Popper-type oxides are also of interest because their alternating perovskite and rock-salt layers may accommodate oxygen non-stoichiometry and provide anisotropic pathways for oxygen transport [23]. Nevertheless, the functional properties of these materials depend strongly on their phase purity, crystallographic distortion, defect chemistry and resistance to alkaline-earth segregation [24,25].

The synthesis method plays a decisive role in determining these characteristics. Even when the same nominal composition is targeted, different preparation routes may produce substantial differences in precursor homogeneity, crystallization temperature, particle size, agglomeration state, specific surface area and secondary-phase content [26]. Conventional solid-state synthesis generally requires prolonged treatment at elevated temperatures, which may favor phase formation but can also promote grain growth, elemental segregation and loss of surface area. Wet-chemical methods, including co-precipitation, sol-gel processing, citrate-nitrate combustion and Pechini-type synthesis, may provide improved mixing of the constituent cations and reduce the diffusion distances required for phase formation [27–32]. However, increasing the number of chemical elements within the same precursor also increases the possibility of non-simultaneous precipitation, selective dissolution, incomplete reaction and local chemical heterogeneity. A systematic evaluation of thermal decomposition, phase evolution and elemental distribution is therefore required before a newly designed composition can be considered for electrode fabrication and electrochemical testing.

Compositionally complex and high-entropy oxides have recently emerged as a possible strategy for expanding the compositional space available for solid oxide cell materials [33–36]. In these systems, several cations are incorporated in comparable proportions within one or more crystallographic sublattices. The associated configurational entropy may contribute to the free-energy balance and can, under suitable conditions, favor the formation of a major disordered crystalline phase. At the same time, the simultaneous presence of cations with different ionic radii, preferred coordination environments and accessible oxidation states produces local lattice distortion and a broad distribution of metal–oxygen bond lengths. These features may alter oxygen-vacancy formation, surface reactivity and transport behavior. Nevertheless, compositionally complex oxides may still contain secondary phases, chemically segregated regions or short-range cation ordering. Moreover, their crystallization behavior is governed not only by configurational entropy but also by precursor chemistry, ionic-size compatibility, charge balance, oxygen stoichiometry and kinetic factors associated with the selected synthesis route.

Within this context, doped lanthanum ferrites provide useful reference systems for evaluating the influence of A-site chemistry on the formation and stability of layered perovskite-related phases. The replacement of Sr^{2+} by Ca^{2+} modifies the average A-site radius, lattice distortion and chemical affinity toward secondary calcium-containing phases. Such substitutions can influence oxygen non-stoichiometry and transport properties, but they may also alter the temperature required for crystallization and the tendency toward alkaline-earth segregation. A direct comparison between Sr- and Ca-containing ferrites prepared through the same wet-chemical route can therefore provide information on the relationship between A-site selection, phase purity and microstructural development.

The present study also examines a compositionally complex Pr–Ba–Ca–Fe–Co–Ni–Cu–Zn oxide containing five nominally equimolar transition-metal species on the B sublattice. This composition was selected to investigate whether extensive B-site mixing can facilitate the formation of a major perovskite-related phase at relatively moderate calcination temperatures while retaining a fine and porous microstructure.

Although doped lanthanum ferrites, Ruddlesden–Popper oxides and high-entropy perovskites have individually been investigated in previous studies, direct comparisons among chemically conventional and compositionally complex systems are often complicated by differences in synthesis route, precursor chemistry, thermal treatment and characterization methodology. Consequently, the relative contributions of composition and processing history to crystallization, structural disorder and morphology remain difficult to distinguish. A comparative study based on a common co-precipitation approach and a

unified characterization workflow can help clarify these relationships and identify both the advantages and the limitations associated with increasing cationic complexity.

Thus, the scientific novelty of the present work lies in the comparative physicochemical assessment of three chemically distinct candidate electrode materials synthesized through the same general co-precipitation strategy: the Sr-containing lanthanum ferrite LSFC, the Ca-containing lanthanum ferrite LCFC and the compositionally complex PBC-HEO system. The contribution of the work is therefore twofold: (i) it provides a direct comparison of the phase-forming behavior of conventional and compositionally complex perovskite-related oxides prepared using a common wet-chemical approach; (ii) it identifies the trade-offs associated with increasing compositional complexity. In particular, establishing these composition–processing–structure relationships is a necessary preliminary step before conductivity, polarization resistance, redox cycling and long-term electrochemical performance can be meaningfully assessed.

Accordingly, the objective of this work is to determine how cation composition and thermal treatment influence the decomposition pathway, phase formation, local structural disorder, elemental distribution and microstructure of co-precipitated perovskite-related oxides. The investigated materials are intended as candidate electrocatalysts for intermediate- to high-temperature reversible solid oxide cells (ReSOCs). These electrochemical devices are designed for applications in the hydrogen and clean energy industry, where they can operate either as solid oxide fuel cells (SOFCs) for efficient electricity generation or as solid oxide electrolysis cells (SOECs) for hydrogen production and renewable energy storage within Power-to-Hydrogen and Power-to-X technologies.

2. Materials and Methods

Three perovskitic electrocatalysts were synthesized via co-precipitation route using sodium hydroxide as precipitating agent. The investigated compositions were two co-doped lanthanum ferrite-based oxides, namely $(\text{La}_{0.8}\text{Sr}_{1.2})(\text{Fe}_{0.9}\text{Co}_{0.1})\text{O}_{6+\delta}$ (labeled as LSFC) and $(\text{La}_{0.8}\text{Ca}_{1.2})(\text{Fe}_{0.9}\text{Co}_{0.1})\text{O}_{6+\delta}$ (labeled as LCFC), and one high-entropy praseodymium nickelate-based oxide, namely $\text{Pr}(\text{Ba}_{0.8}\text{Ca}_{0.2})(\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})_2\text{O}_{6+\delta}$ (labeled as PBC-HEO).

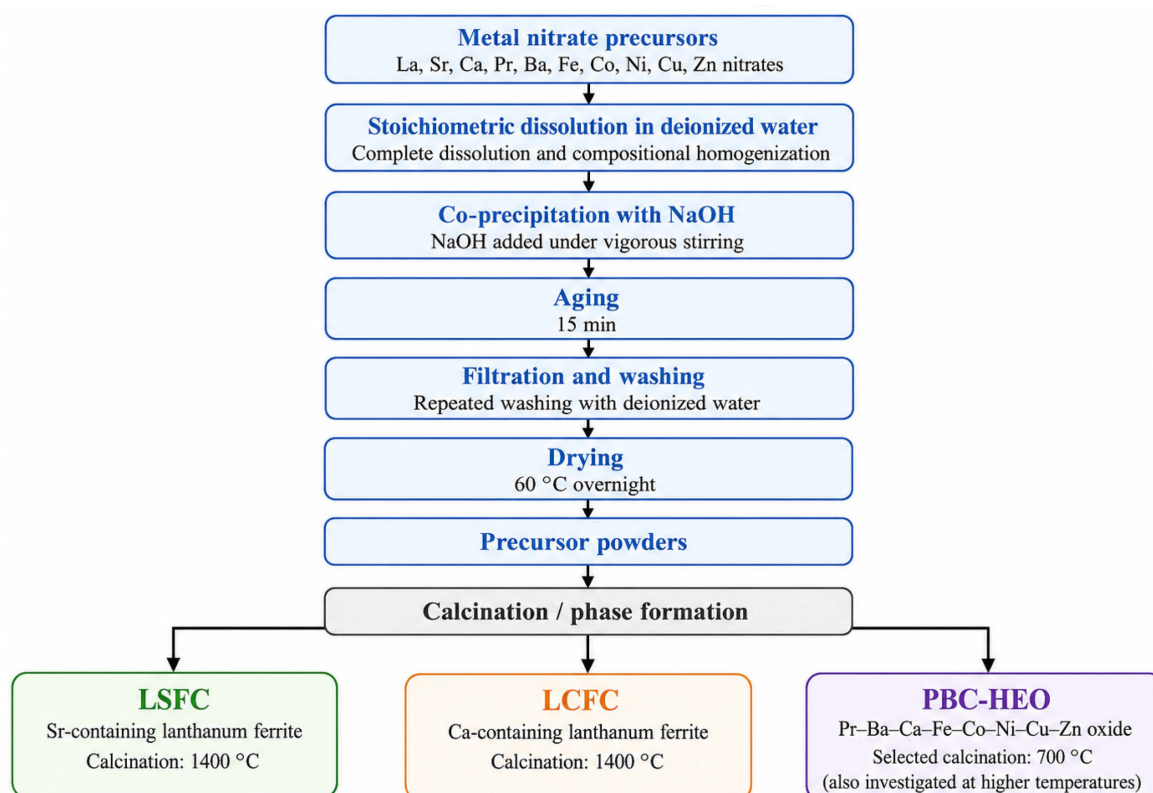
2.1. Synthesis Procedure and Main Process Parameters

The investigated perovskite-related powders were synthesized through an aqueous co-precipitation route using analytical-grade metal nitrates as cation precursors and sodium hydroxide as the precipitating agent. The precursor solutions were prepared by dissolving stoichiometric amounts of the required La, Sr, Ca, Pr, Ba, Fe, Co, Ni, Cu and Zn nitrates (Sigma Aldrich, Milan, Italy, purity > 99%) in deionized water according to the nominal composition of each material. The solutions were stirred until complete dissolution was achieved, with particular attention paid to the homogenization of the multi-cationic PBC-HEO precursor solution.

Precipitation was induced by adding an aqueous NaOH (Sigma Aldrich, Milan, Italy, purity > 99%) solution to the mixed-metal nitrate solution under vigorous stirring. After completion of the base addition, the resulting suspension was maintained under continuous stirring for an additional aging period of 15 min to promote precipitation completion and improve the chemical homogeneity of the precursor. In fact, since the different cations exhibit distinct hydrolysis equilibria and solubility products, their precipitation may occur at slightly different rates, potentially producing local compositional heterogeneity in highly multicomponent systems. The adopted aging step favors completion of precipitation and partial cation redistribution within the precursor.

The solid product was subsequently separated by filtration and repeatedly washed with deionized water to remove residual nitrate and sodium ions. The recovered precipitate was dried in air at 60 °C overnight, producing the as-prepared precursor powder.

The dried precursors were thermally treated in air to decompose residual hydroxide and nitrate species and induce crystallization of the target oxide phases. The calcination conditions were selected separately for each composition on the basis of the thermal and structural analyses (as discussed in the following paragraphs). LSFC and LCFC were calcined at 1400 °C, whereas the thermal evolution of PBC-HEO was investigated through sequential treatments at 700, 900, 1100 and 1300 °C. After calcination, the powders were manually ground in an agate mortar to break down soft agglomerates and obtain homogeneous powders suitable for subsequent characterization. The following Scheme 1 summarizes the adopted fabrication process for all three investigated materials.



Scheme 1. Production flowchart of the investigated materials.

The following Table 1 shows the details of the chemical formulas and the identifiers of all the samples, both pre- and post-heat treatment; while the following Table 2 presents the main process parameters used for the synthesis of the investigated materials.

Table 1. Composition of all systems with their labelling and treatment cycles.

Chemical Composition	Labelling	Number of Samples	Calcination Cycles
$(\text{La}_{0.8}\text{Sr}_{1.2})(\text{Fe}_{0.9}\text{Co}_{0.1})\text{O}_{6+\delta}$	LSFC	2	1400 °C for 8 h
$(\text{La}_{0.8}\text{Ca}_{1.2})(\text{Fe}_{0.9}\text{Co}_{0.1})\text{O}_{6+\delta}$	LCFC	3	1400 °C for 8 h
$\text{Pr}(\text{Ba}_{0.8}\text{Ca}_{0.2})(\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})_2\text{O}_{6+\delta}$	PBC-HEO	3	700 °C for 2 h 900 °C for 2 h 1100 °C for 2 h 1300 °C for 2 h

Table 2. Main process parameters adopted for the synthesis of the investigated systems.

Synthesis Step	Process Parameters	Adopted Value
Solutions preparation	Total metal-ion concentration	0.1 M
Solutions preparation	Precipitating agent concentration	4 M
Precipitation	Precipitating solution addition rate	∞ (very fast)
Precipitation	Final pH	13–14
Aging	Stirring rate	300 rpm
Washing/Filtration	Number of washing cycles	3
Drying	Temperature	60 °C
Calcination	Heating rate	10 °C/min
Calcination	Cooling rate	Free cooling
Calcination	Calcination atmosphere	Air
Calcination	Crucible material	High-purity alumina

2.2. Materials Characterization

All systems were characterized in terms of crystalline structure and phase composition by XRD, using a Panalytical X'PERT MPD diffractometer (Malvern Panalytical S.r.l., Via Guglielmo Oberdan 36, 20851 Lissone (MB), Italy).

The thermal behavior of the as-precipitates was examined through Differential Thermal Analysis and Thermogravimetric Analysis (DTA-TG) by using a Netzsch (NETZSCH Group, Gebrüder-Netzsch-Straße 19, 95100 Selb, Germany) STA 409 thermal analyzer up to 1400 °C (by using a heating rate of 10 °C/min).

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used to assess the elemental composition of the synthesized electrolytes and electrocatalysts and check their consistency with the nominal composition. Samples were prepared with a CH-DIG8 digestion unit. Approximately 0.010 g of sample powder was digested in aqua regia and analyzed with a Thermo Scientific (Thermo Fisher Scientific, 168 Third Avenue, Waltham, MA 02451, USA) iCAP RQ ICP-MS. Measurements were acquired in both standard mode (STD) and kinetic energy discrimination mode (KED). Calibration standards were prepared from commercially available certified reference solutions. Rare-earth elements and related analytes were calibrated using an Agilent (Agilent Technologies Italia SpA, Milan, Italy, Via Piero Gobetti 2/c, 20063 Cernusco sul Naviglio (MI)) ICP-MS calibration standard IMS-101, containing 17 elements at nominal concentrations of 10 µg/mL in 5% nitric acid: Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Sc, Tb, Th, Tm, Yb and Y. For the calibration of the remaining major and trace elements, an ICP Multi-Element Standard Solution VIII (Merck, Darmstadt, Germany) was used. This standard contained 22 elements in dilute nitric acid: Al, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr, Te, Tl and Zn. For each sample, six replicate measurements were acquired for each isotope; for each set of six measurements, the mean concentration, standard deviation (SD) and relative standard deviation (RSD) were calculated from the raw data. Each sample was analyzed in two separate injection blocks, and the final concentration of each isotope was calculated as the mean of the two block-specific mean concentrations. The SD and RSD calculated from the two-block means were used to describe between-block variability. Concentrations were

corrected by the additional 1:500 dilution performed before instrumental analysis. All concentrations were subsequently expressed in ppb to ensure consistency among analytes. Subsequently, measurements were performed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), using a Thermo Scientific (Thermo Fisher Scientific, 168 Third Avenue, Waltham, MA 02451, USA) iCap 7000 Series spectrometer. The same analytical standards and sample solutions used for ICP-MS measurements were used. In order to avoid detector saturation for alkaline-earth metals, iron, nickel and rare earth elements, a further 1:100 dilution was performed on the samples. The spectrometer was previously calibrated for quantitative analysis with five standard solutions containing known elements concentrations: 0.001, 0.01, 0.1, 1.0, and 10.0 mg/L. The calibration lines showed a correlation coefficient greater than 0.99. For each set of three measurements, the mean concentration, the standard deviation (SD) and relative standard deviation (RSD) were calculated from the raw data. The resulting elemental concentrations were expressed as ppm (mg/kg of sample weight).

The microstructural characterization and local chemical analysis of the calcined electrocatalyst powders were performed by Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS), using a JEOL JSM-IT210 instrument (JEOL Ltd., Tokyo, Japan) operated in high-vacuum mode. Surface morphology was investigated by means of a secondary electron detector (SED), which provides topographic contrast at high spatial resolution. Qualitative and quantitative elemental microanalysis was carried out by point EDS spectra acquired on selected areas of the samples, while the spatial distribution of the constituent elements was assessed through full-area elemental mapping. All analyses were performed at an accelerating voltage of 20.0 kV and a working distance of 10.0 mm. EDS quantification was performed using a standardless method based on the ZAF matrix correction algorithm (Z: atomic number correction, A: absorption correction, F: fluorescence correction).

Infrared spectra of the various samples were acquired with a Perkin Elmer Spectrum One FTIR spectrometer equipped with a universal Attenuated Total Reflectance (ATR) apparatus (GladiATR, Pike technologies). The internal reflection element was a single-bounce diamond microprism with a diameter of 4 mm. The powders were pressed onto the ATR crystal and 16 interferograms were acquired and averaged. The resolution of all spectra was set at 4 cm^{-1} .

Raman investigations were conducted using a Horiba equipped with an Xplora (Xplora Technologies AS, Nedre Slottsgate 8, 0157 Oslo, Norway) microRaman microscope. Excitation was provided by a 638 nm diode laser focused on the sample through a $100\times$ objective. Spectral acquisition consisted of 128 accumulations. The scattered light was dispersed using a 1200 L/mm grating, yielding a spectral resolution of approximately 6 cm^{-1} .

3. Results and Discussion

DTA–TG analyses were first performed on the as-prepared precursors to investigate their thermal evolution and to define suitable calcination conditions for the formation of the target perovskitic phases. The thermal profiles of the LSFC and LCFC systems showed relatively simple decomposition pathways and are therefore not reported here. Conversely, the PBC-HEO precursor displayed a very complex thermal behavior, as shown in the following Figure 1.

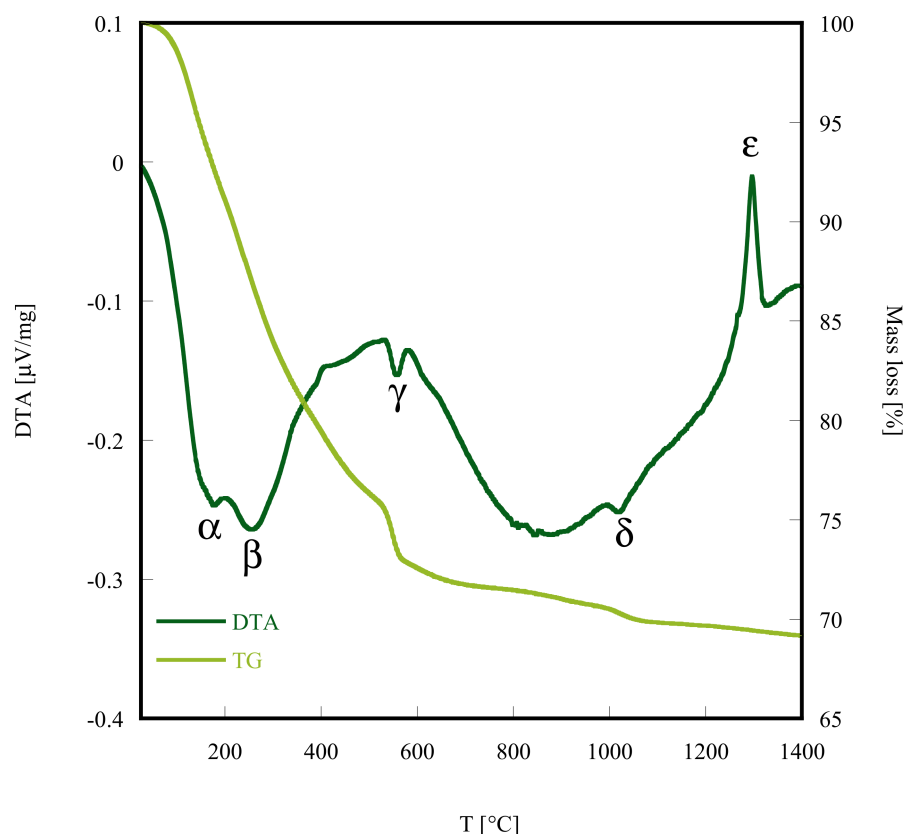


Figure 1. DTA/TG curves of the as-synthesized PBC-HEO sample.

The DTA curve in Figure 1 exhibits five main events. The first two events are marked by endothermic peaks (α and β) at approximately 170 and 250 °C, accompanied by substantial and continuous mass losses amounting to nearly 25%, which can be ascribed to the release of adsorbed moisture and crystallization water, respectively [37]. The third endothermic peak (γ) observed at around 530 °C can be associated with the decomposition of residual as-precipitated hydroxides, in agreement with the diffraction patterns shown in the following subsection. At higher temperatures, a small endothermic peak is observed around 1050 °C. This event can be associated with the reduction of trivalent cations (transition metals, mainly Ni and Co) formed during the thermal treatment with the simultaneous small weight loss associated to $O_2(g)$ evolution [37], revealed clearly in the TG curve in Figure 1. Finally, at around 1300 °C, a sharp exothermic peak (ϵ) is observed in Figure 1, associated with no evident mass loss. To support the interpretation of such high-temperature peak, a detailed structural analysis (see Figure 2) of the PBC-HEO has been carried out and discussed hereafter.

The as-synthesized PBC-HEO sample is poorly crystallized as only a few extremely broad peaks are visible (see Figure 2A), likely attributable to a mixture of different as-precipitated hydroxides and/or hydrated oxides. Upon calcination at 700 °C (for 2 h), i.e., after the γ peak in the DTA-TG curve, a major orthorhombic praseodymium nickelate-like phase (ICDD card n. 01-079-2455) is formed, along with traces of a secondary hexagonal zinc oxide phase (ICDD card n. 01-075-0576), whose peak are labeled with $\circ$ in Figure 2. At a calcination temperature of 900 °C (Figure 2C), almost no difference is observed, while at higher calcination temperatures (i.e., 1100 °C and 1200 °C) the relative intensity of the reflections assigned to the secondary phase amount of secondary zinc oxide-like phase increased significantly. Finally, at a calcination temperature of 1300 °C, i.e., around the exothermic ϵ peak in Figure 1, PBC-HEO-1300 exhibited markedly different behavior from the other calcined PBC-HEO samples. In fact, its diffraction pattern exhibits a broad amor-

phous halo along with some of the most intense peaks of the orthorhombic praseodymium nickelate-like phase (ICDD card n. 01-079-2455).

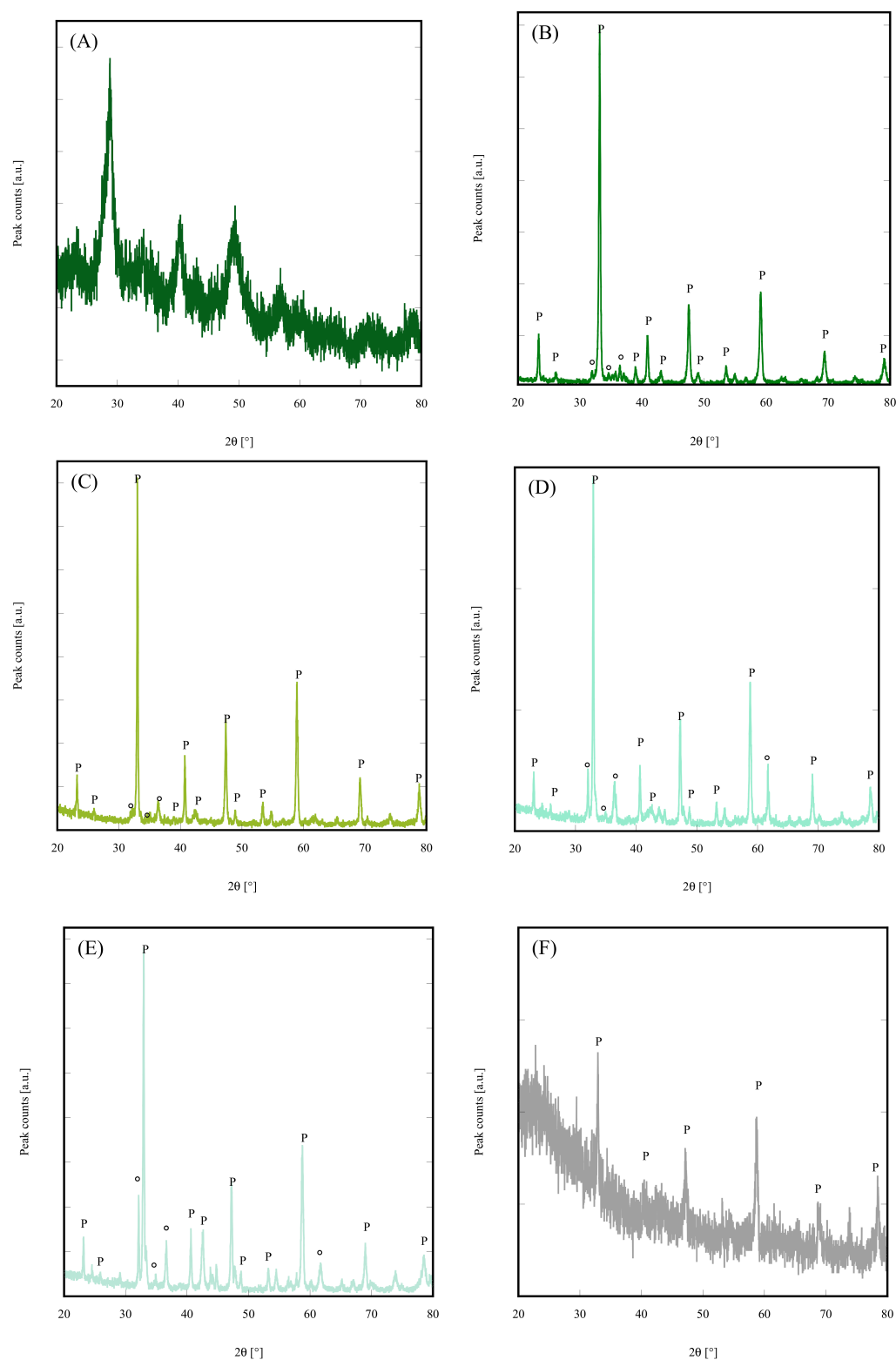


Figure 2. XRD patterns of the PBC-HEO samples: as-synthesized (A), calcined at 700 °C (B), calcined at 900 °C (C), calcined at 1100 °C (D), calcined at 1200 °C (E) and calcined at 1300 °C (F). P denote peaks attributable to a major orthorhombic praseodymium nickelate-like phase (ICDD card n. 01-079-2455); ° denote peaks attributable to a minor hexagonal zinc oxide phase (ICDD card n. 01-075-0576).

Additional experiments demonstrated that extensive liquid-phase formation occurs in the multicomponent PBC-HEO system at high temperature. In particular, a pellet treated at 1400 °C underwent macroscopic deformation and yielded solidified shards. XRD analysis of the recovered and pulverized material revealed a biphasic systems (Figure S1) consisting of a tetragonal perovskite-related phase and a fluorite-type phase, indicating that the high-temperature process involves decomposition and structural reconstruction rather than simple incorporation of the secondary Zn-rich phase into the original lattice. Moreover, the approximately 1300 °C exothermic peak was absent when Zn was replaced by Cr and when Ba was replaced by Sr in two additional HEO systems (Figures S2 and S3), suggesting that the ϵ event is specifically associated with the combined presence of Ba and Zn. The peak may therefore originate from an exothermic Ba–Zn-dependent solid-state reaction, the formation of a transient Ba–Zn–O intermediate, or crystallization/phase separation associated with a transient Ba–Zn-rich oxide liquid. The precise mechanism and composition of the high-temperature phases cannot be resolved from the present ex-situ data and it is outside the scope of the present work.

The ideal configurational entropy of the PBC-HEO nominal composition was evaluated by considering the crystallographic sublattices separately. The five equimolar B-site cations provide a configurational entropy of $R \ln 5 = 1.609R$ per mole of B sites. Considering two B sites per formula unit and assuming an A-site-ordered structure in which Ba and Ca randomly share one A' sublattice, the total ideal configurational entropy of PBC-HEO is $3.719R$. The composition-weighted Shannon radii [38] give an average A-site radius of 1.438 Å and an average B-site radius of approximately 0.683 Å under the adopted working oxidation-state model. The corresponding Goldschmidt tolerance factor [39] for PBC-HEO is 0.963, while the B-site ionic-radius mismatch is approximately 7.3%, indicating geometric compatibility with a cubic perovskite-related framework. However, the Goldschmidt factor has already been proven not sufficient to predict high-entropy perovskites equilibrium structures [35]. Definitely, these calculations demonstrate a potentially significant configurational-entropy contribution and favorable geometric compatibility, even if they do not independently prove entropy-driven reversible stabilization.

Figure 3 presents the diffraction patterns of the LCFC and LSFC systems, both as-prepared and calcined at 1300 and 1400 °C [34–36]. In all cases, the as-prepared powders are mostly amorphous with several broad peaks attributable to single hydroxides. Conversely, calcined LCFC and LSFC showed a different structural behavior, with the former never obtained as single-phase perovskite, and the latter obtained as single-phase perovskite only after calcination at 1400 °C for 6 h. Particularly, both LCFC-1300 and LCFC-1400 are mainly formed by an orthorhombic lanthanum/calcium ferrite (ICDD card n. 00-049-1885) and a secondary calcium oxide phase (whose main peaks are labeled with # in Figure 3A,B). Conversely, LSFC-1300 is formed by a mixture of two different tetragonal perovskites (ICDD card n. 01-070-1733 and n. 00-032-1237), while LSFC-1400 is formed by a pure orthorhombic lanthanum/strontium cobalt ferrite (ICDD card. n. 01-089-1268).

Summarizing, after calcination at 1400 °C, LSFC crystallized as a single orthorhombic La–Sr–Fe–Co oxide phase, indexed according to ICDD card No. 01-089-1268. LCFC predominantly exhibited an orthorhombic La–Ca ferrite structure, indexed according to ICDD card No. 00-049-1885, together with a residual Ca-containing secondary phase. PBC-HEO calcined at 700 °C consisted predominantly of an orthorhombic praseodymium-nickelate-like phase, indexed according to ICDD card No. 01-079-2455, accompanied by a minor hexagonal ZnO-type secondary phase, indexed according to ICDD card No. 01-075-0576. The residual Ca-containing phase in LCFC and the Zn-rich secondary phase in PBC-HEO may affect electrical transport, interfacial compatibility and long-term electrode stability. Their precise phase fractions could not be reliably quantified from the available diffrac-

tion data and should be determined in future work using higher-resolution diffraction measurements.

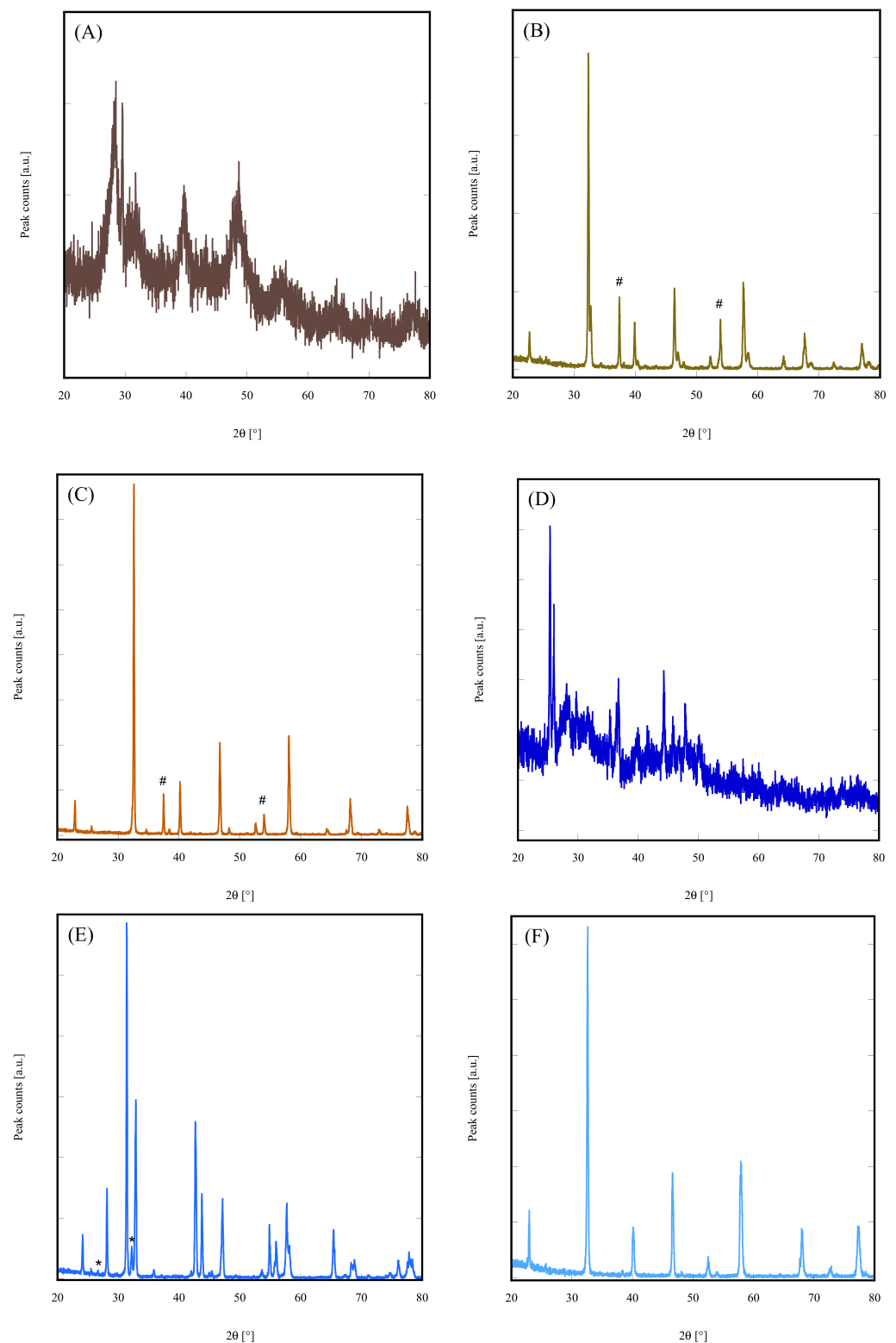


Figure 3. XRD patterns of the LCFC samples: as-synthesized (A), calcined at 1300 °C (B) and calcined at 1400 °C (C); and of the LSFC samples: as-synthesized (D), calcined at 1300 °C (E) and calcined at 1400 °C (F). # highlights peak attributable to minor Ca-containing secondary phase, while * highlights peak attributable to a secondary unidentified phase.

3.1. Vibrational Spectroscopy (Raman and FTIR)

Raman and FTIR spectroscopy were employed to investigate the local structure, bonding environment and degree of disorder of the synthesized electrocatalysts.

All samples exhibited characteristic metal–oxygen vibrational modes associated with perovskite-type structures, confirming the successful formation of the targeted oxide frameworks.

As discussed in Section 1, ABO_3 -type perovskites accommodate cation substitution at both the A and B sites. However, the A:B stoichiometric ratio of 2:1 in LSFC and LCFC (Table 1) is characteristic not of a simple three-dimensional ABO_3 perovskite, but of an $n = 1$ Ruddlesden–Popper (RP) phase, $\text{A}_2\text{BO}_{4+\delta}$, in which single perovskite-type BO_6 layers alternate with rock-salt-type AO layers along the crystallographic c-axis [40–42]. In this layered architecture, the B-site cation is coordinated by two structurally inequivalent oxygen types, four equatorial oxygens within the perovskite layer and two apical oxygens pointing toward the adjacent rock-salt layer, the latter being typically more weakly bound and more sensitive to A-site substitution [41,42]. PBC-HEO, by contrast, crystallizes as a three-dimensional double-perovskite-type nickelate (Section 3.2), where the BO_6 octahedra form a fully connected network without this layered anisotropy.

Figure 4 compares the baseline-corrected, smoothed Raman spectra of LSFC, LCFC and PBC-HEO in the $400\text{--}800\text{ cm}^{-1}$ range. All three samples display a common lower-frequency envelope ($450\text{--}620\text{ cm}^{-1}$), attributable to octahedral bending/tilting vibrations, together with a dominant higher-frequency envelope ($650\text{--}770\text{ cm}^{-1}$), attributable to BO_6 stretching. The stretching envelope, however, differs markedly in shape among the three systems—peaking at lower frequency in LSFC, at higher frequency in LCFC, and appearing broader and more symmetric in PBC-HEO—suggesting that it is not a single vibrational mode but the superposition of at least two overlapping components with sample-dependent relative weight.

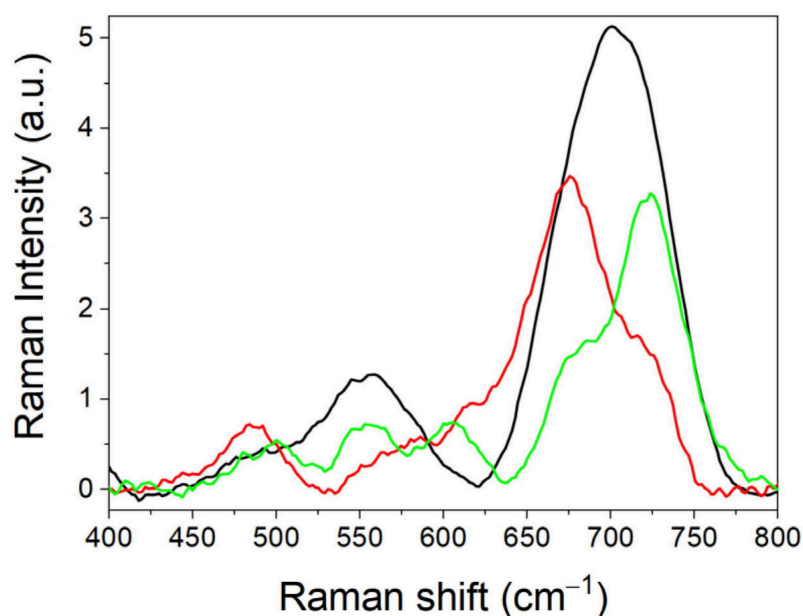


Figure 4. Baseline-corrected and smoothed Raman spectra of LSFC (red line), LCFC (green line) and PBC-HEO (black line) in the $400\text{--}800\text{ cm}^{-1}$ range, showing the common bending/tilting envelope ($450\text{--}620\text{ cm}^{-1}$) and the compositionally dependent stretching envelope ($650\text{--}770\text{ cm}^{-1}$).

This was confirmed by multi-peak pseudo-Voigt deconvolution of each spectrum (Figure 5a–c; $R^2 = 0.998\text{--}0.999$ in all cases), which resolved the stretching envelope into two sub-modes centered at $\sim 676\text{--}681\text{ cm}^{-1}$ and $\sim 718\text{--}725\text{ cm}^{-1}$ in all three samples.

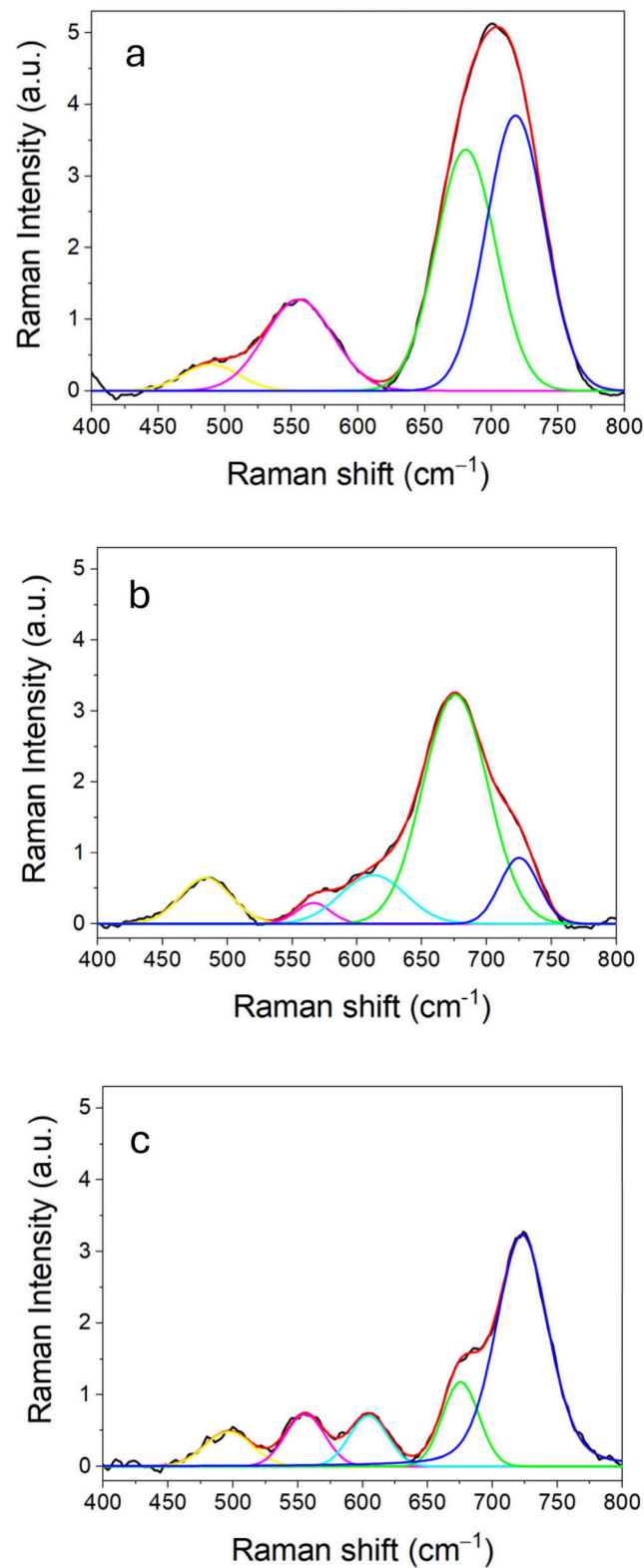


Figure 5. Multi-peak pseudo-Voigt deconvolution ($R^2 = 0.998\text{--}0.999$) of the Raman spectra of (a) PBC-HEO, (b) LSFC and (c) LCFC (black, experimental data; red, overall fit), resolving three bending/tilting components at ~ 500 (yellow), ~ 550 (magenta) and $\sim 600\text{ cm}^{-1}$ (cyan, absent in PBC-HEO), and two BO_6 stretching sub-modes at $\sim 675\text{--}680$ (green) and $\sim 715\text{--}725\text{ cm}^{-1}$ (blue), the latter assigned to equatorial and apical Fe–O stretching in the RP ferrites LSFC/LCFC.

In LSFC and LCFC, these are assigned to the equatorial and apical Fe–O stretching modes expected for an $n = 1$ RP structure [41–44]; in PBC-HEO, which lacks this layered

anisotropy, the analogous splitting more likely reflects two symmetry-related stretching components arising from B-site configurational disorder. The three electrocatalysts are distinguished less by the overall bandwidth of this envelope than by the relative weight of its two components: the lower-frequency sub-mode dominates in LSFC (amplitude ratio ≈ 3.4 , area ratio ≈ 5.9), the higher-frequency one dominates in LCFC instead (amplitude ratio ≈ 0.36 , area ratio ≈ 0.22), while PBC-HEO shows a near-balanced contribution from both (ratio ≈ 0.9)—explaining its broader, more symmetric envelope in Figure 4. For the RP ferrites, this redistribution tracks the A-site ionic radius: the larger Sr^{2+} [45] preferentially elongates and softens the apical Fe–O bond, shifting weight toward the lower-frequency component, whereas the smaller Ca^{2+} shortens and stiffens the same bond, favoring the higher-frequency component. The near-equal partitioning in PBC-HEO instead reflects the coexistence of five different B-site transition-metal cations, which prevents either component from dominating.

The same deconvolution also resolved the lower-frequency bending/tilting region ($450\text{--}620\text{ cm}^{-1}$) into several components. Both RP ferrites display three well-resolved modes in this region (LSFC: $\sim 483, 566, 612\text{ cm}^{-1}$; LCFC: $\sim 497, 556, 604\text{ cm}^{-1}$), consistent with octahedral tilting typical of orthorhombic RP-type ferrites regardless of the A-site dopant. PBC-HEO instead shows only two resolved components ($\sim 489, 556\text{ cm}^{-1}$), reflecting its distinct three-dimensional double-perovskite structure and correspondingly different vibrational selection rules, rather than a simple increase or decrease in structural distortion relative to the layered ferrites [46–48].

Taken together, these results indicate that composition governs the Raman response of these electrocatalysts primarily through the redistribution of spectral weight between apical/equatorial (or symmetry-related) stretching sub-modes and through the multiplicity of octahedral tilting modes, rather than through a simple monotonic trend in bandwidth—linking the observed spectra directly to the distinct defect-chemical mechanisms at play in each system (A-site-driven apical bond softening/stiffening in the RP ferrites; B-site configurational disorder in the compositionally complex PBC-HEO).

Finally, FTIR analysis (see Supplementary Materials) further confirmed the formation of a double-perovskite structure, characterized by intense M–O absorption bands in the $450\text{--}700\text{ cm}^{-1}$ region and only minor traces of surface carbonates.

3.2. Chemical Composition (ICP-MS and ICP-OES)

Table 3 summarizes the measured composition *vs.* the nominal one of all the studied systems. ICP-MS and ICP-OES data for the samples are reported in Supplementary Tables S1 and S2, respectively.

Table 3. Measured composition *vs.* nominal composition for electrocatalysts. LSFC and LCFC calcined at $1400\text{ }^{\circ}\text{C}$, PBC-HEO calcined at $700\text{ }^{\circ}\text{C}$.

Sample	Nominal Composition	Measured Composition (ICP-MS)	Measured Composition (ICP-OES)
LCFC	$(\text{La}_{0.8}\text{Ca}_{1.2})(\text{Fe}_{0.9}\text{Co}_{0.1})\text{O}_{6+\delta}$	$(\text{La}_{0.7}\text{Ca}_x)(\text{Fe}_{0.7}\text{Co}_{0.1})\text{O}_{6+\delta}$	$(\text{La}_{0.75}\text{Ca}_{0.75})(\text{Fe}_{0.88}\text{Co}_{0.10})\text{O}_{6+\delta}$
LSFC	$(\text{La}_{0.8}\text{Sr}_{1.2})(\text{Fe}_{0.9}\text{Co}_{0.1})\text{O}_{6+\delta}$	$(\text{La}_{0.7}\text{Sr}_{0.2})(\text{Fe}_{0.8}\text{Co}_{0.1})\text{O}_{6+\delta}$	$(\text{La}_{0.91}\text{Sr}_{0.15})(\text{Fe}_{0.88}\text{Co}_{0.10})\text{O}_{6+\delta}$
PBC-HEO	$\text{Pr}(\text{Ba}_{0.8}\text{Ca}_{0.2})(\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})_2\text{O}_{6+\delta}$	$\text{Pr}_{0.85}(\text{Ba}_{0.01}\text{Ca}_{0.1})(\text{Fe}_{0.1}\text{Co}_{0.2}\text{Ni}_{0.5}\text{Cu}_{0.2}\text{Zn}_{0.2})_2\text{O}_{6+\delta}$	$\text{Pr}_{0.67}(\text{Ba}_{0.03}\text{Ca}_{0.16})(\text{Fe}_{0.20}\text{Co}_{0.20}\text{Ni}_{0.20}\text{Cu}_{0.20}\text{Zn}_{0.19})_2\text{O}_{6+\delta}$

ICP-MS analysis was performed on calcined LCFC, LSFC, and PBC-HEO (calcined at $1400\text{ }^{\circ}\text{C}$ and $700\text{ }^{\circ}\text{C}$, respectively) samples. For all samples, moles were calculated by dividing elemental concentrations (ppm) by atomic mass; subsequently molar ratios were determined normalized to the element with the lowest nominal stoichiometric coefficient.

LCFC measured composition is very close to the nominal composition, with a ratio La:Fe:Co of 0.66:0.73:0.10, versus a nominal ratio of 0.8:0.9:0.1.

The measured composition of LSFC shows a La:Sr:Fe:Co ratio of 0.69:0.16:0.82:0.10 vs. nominal coefficients of 0.8:1.2:0.9:0.1. In this case, the measured Sr appears to be 7.5 times lower than the expected mole ratio, in stark contrast with the results obtained with SEM-EDX (*vide infra*), suggesting strong matrix effects.

Regarding the compositionally complex electrocatalyst PBC-HEO, the measured ratios of Pr:Ba:Fe:Co:Ni:Cu:Zn are 0.85:0.03:0.23:0.40:0.46:0.37:0.33, compared with the nominal ratio of 1:0.8:0.4:0.4:0.4:0.4:0.4. The ratios were calculated considering that the (FeCoNiCuZn) unit has a 2 to 1 ratio with the Pr and (BaCa) units. As in the previous sample for Sr, the alkaline-earth element Ba shows a surprisingly low ratio, while all the transition metal and praseodymium are close to the expected value.

The anomalously low Sr and Ba contents obtained by ICP-MS should therefore be interpreted with caution and are most likely related to matrix-dependent limitations of the aqua regia digestion rather than to an actual large deviation from the nominal stoichiometry; indeed, aqua regia-based protocols may provide only pseudo-total dissolution of refractory oxide/perovskite matrices, while alkaline-earth elements, especially Ba, may suffer from incomplete recovery due to poor solubilization and/or precipitation phenomena involving sulfate, carbonate, phosphate, fluoride or chromate species [49,50].

In summary, the ICP-MS analysis confirms the close adherence of the synthetic methods to the expected elemental rare-earth composition, with the slightly lower values for La and Pr that could be attributed to the presence of ReO^+ ions, whose mass is detected as that of a Gd isotope.

The same calculations on stoichiometry were performed using ICP-OES data. The measured composition of LCFC is even closer to the nominal composition, with a ratio La:Fe:Co:Ca of 0.75:0.88:0.10:0.75, versus a nominal ratio of 0.8:0.9:0.1:1.2, except for Ca, which, while more soluble than Ba and Sr, nevertheless suffers from the formation of insoluble salts.

The measured composition of LSFC shows a La:Sr:Fe:Co ratio of 0.91:0.15:0.88:0.10 vs. nominal coefficients of 0.8:1.2:0.9:0.1, confirming the matrix effects on Sr previously mentioned, while affording satisfactory measurements for the other elements.

Regarding the compositionally complex electrocatalyst PBC-HEO, the measured ratios of Pr:Ba:Fe:Co:Ni:Cu:Zn:Ca are 0.67:0.03:0.40:0.40:0.39:0.40:0.38:0.16, compared with the nominal ratio of 1:0.8:0.4:0.4:0.4:0.4:0.4:0, essentially reproducing the results observed in ICP-MS data, but with lower concentrations for Pr and better correspondence for Fe. As in the previous sample for Sr, the alkaline-earth element Ba shows a surprisingly low ratio, while calcium, all transition metals and praseodymium are close to the nominal ratios.

Despite the known limitations of aqua regia digestion for alkaline-earth elements, the concordance between ICP-MS and ICP-OES results provides convincing evidence of the overall stoichiometric integrity of the synthesized materials. The slight inconsistency among rare earth readings between techniques may reflect technique-dependent interference effects.

3.3. Morphology and Elemental Distribution (SEM-EDX)

Representative SEM micrographs and EDX elemental analyses of the synthesized electrocatalysts are shown in Figures 6 and 7, respectively.

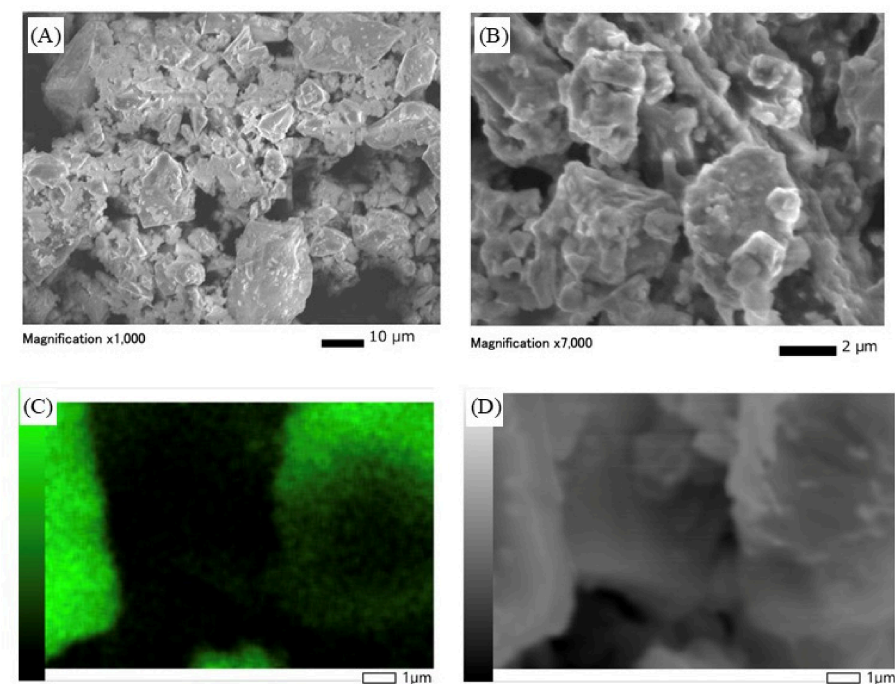


Figure 6. LCFC SEM $\times 1000$ (A) and SEM $\times 7000$ (B), showing polyhedral agglomerates with heterogeneous particle sizes; EDS mapping at $\times 15,000$, with the Sr-L map presented in panel (C), showing local enrichment; IMG1(1st) as a morphological context (D).

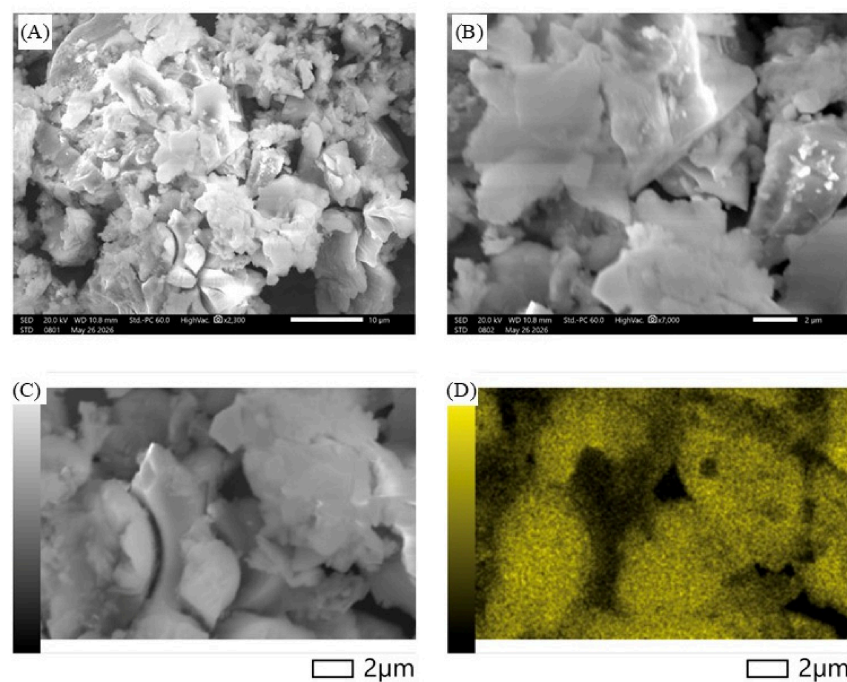


Figure 7. LSFC SEM $\times 2300$ (A) and SEM $\times 7000$ (B), showing interconnected open porosity and individual sub-micrometer roughness and grains; IMG1(1st) as a morphological context (C); EDS mapping at $\times 5000$, panel Ca-K map (D), showing local segregation of calcium.

The LSFC catalyst (Figure 7A) exhibited polyhedral agglomerates with heterogeneous particle sizes ranging from approximately 1 μm to over 10 μm . Higher-magnification observations revealed dense surfaces composed of partially sintered sub-grains with dimensions between 200 and 800 nm. The corresponding EDXS analysis (Figure 6B) indicated that, although local Sr enrichment [51] was detected in some regions, selected areas main-

tained the Sr/La ratios very close to the nominal composition, confirming a generally good preservation of the target stoichiometry [52].

The LCFC catalyst showed agglomerates composed of submicrometric grains with rough and irregular surfaces (Figure 7A). A relatively homogeneous open porosity was observed throughout the sample. EDXS results (Figure 7B,C) revealed local calcium-rich regions and evidence of surface carbonation, in agreement with the tendency of calcium-containing oxides to react with atmospheric CO₂ to form calcium carbonate [53].

Interestingly, PBC-HEO exhibited the most developed porous architecture (Figure 8A). Its microstructure consisted of interconnected submicrometric grains (150–500 nm) separated by a dense network of open pores and diffusion channels. Such morphology seems particularly advantageous for electrochemical applications because it maximizes the active surface area and facilitates mass transport. However, the corresponding EDX analysis (Figure 8B,C) revealed significant compositional heterogeneity, including segregated regions enriched in Ni and Cu (very likely corresponding to the secondary phase observed in the corresponding diffractogram), indicating incomplete elemental homogenization despite the favorable microstructural features [54]. Furthermore, the PBC-HEO SEM micrographs indicate an open network of coalesced submicrometric grains of about 150–500 nm, interconnected voids, and sintering necks. From a qualitative morphological perspective, this architecture may facilitate gas penetration through the powder layer and provide a comparatively large accessible solid–gas interface. Nevertheless, SEM imaging does not provide a quantitative measurement of total porosity, pore-size distribution, or specific surface area. Therefore, no direct conclusion regarding enhanced electrocatalytic activity can be derived solely from these observations.

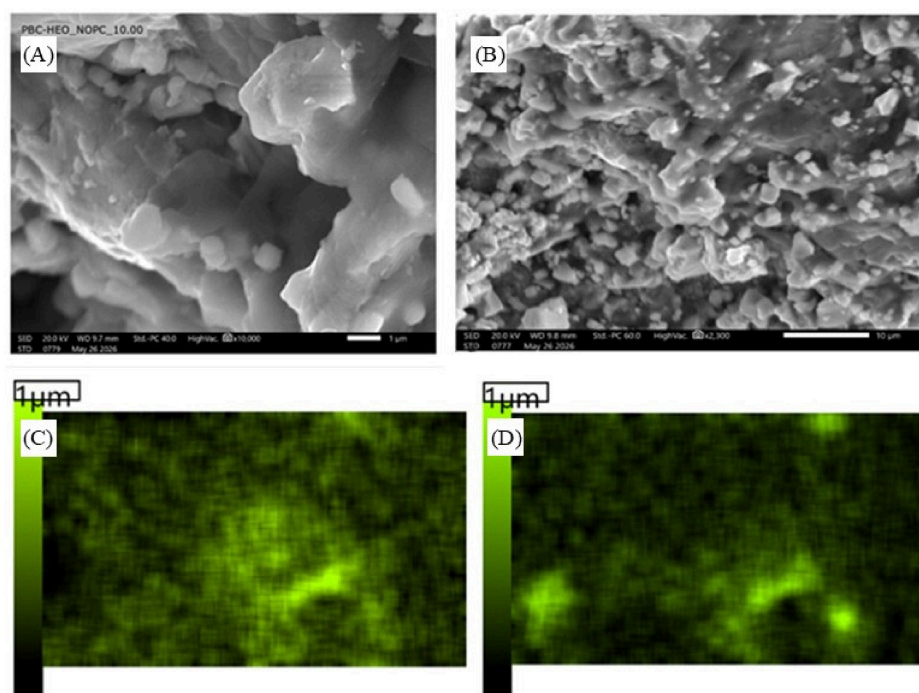


Figure 8. PBC-HEO SEM $\times 10,000$ (A) and SEM $\times 2300$ (B), showing a network of coalesced grains with sintering necks and nanostructured porosity; EDS mapping at $\times 5000$, panels Ni-K (C) and Cu-K (D), showing small areas of localized nickel and copper accumulation.

Summarizing, LSFC consisted of polyhedral agglomerates approximately 1–10 μm in size, and occasionally larger, composed of partially sintered sub-grains with characteristic dimensions of approximately 200–800 nm. LCFC consisted of irregular agglomerates formed by submicrometric grains, generally smaller than 1 μm . PBC-HEO showed the finest

microstructure, consisting of interconnected and partially coalesced grains approximately 150–500 nm in size.

Quantitative EDS spot analyses (Table 4) further confirmed the elemental composition of the three electrocatalysts and provided additional information on their local chemical homogeneity. For the LSFC sample, La, Sr, Fe and Co were detected in proportions consistent with the intended composition, indicating that the high-temperature calcination promoted an almost homogeneous distribution of the constituent cations. This finding is in good agreement with the XRD results, which evidenced the formation of a single-phase perovskite after calcination at 1400 °C, and supports the qualitative elemental maps shown in Figure 6. Moreover, the local Sr content determined by EDS is considerably higher than that measured by ICP-MS, confirming that the anomalously low Sr concentration obtained by bulk analysis is most likely related to incomplete recovery during acid digestion rather than to an actual depletion of strontium in the material.

Table 4. Quantitative EDS analysis of representative regions of the synthesized electrocatalysts: PBC-HEO (a), LSFC (b), LCFC (c). Elemental composition is reported as mass% and atomic% (mean $\pm$ standard deviation) obtained from spot analyses performed on selected areas of the calcined samples.

(a)			
Element	Line	Mass%	Atom%
C	K	2.40 $\pm$ 0.03	8.84 $\pm$ 0.11
O	K	19.34 $\pm$ 0.10	53.49 $\pm$ 0.28
Ca	K	0.33 $\pm$ 0.02	0.36 $\pm$ 0.03
Fe	K	8.63 $\pm$ 0.10	6.84 $\pm$ 0.08
Co	K	7.88 $\pm$ 0.11	5.92 $\pm$ 0.08
Ni	K	6.59 $\pm$ 0.11	4.97 $\pm$ 0.08
Cu	K	2.22 $\pm$ 0.08	1.54 $\pm$ 0.05
Zn	K	4.00 $\pm$ 0.11	2.71 $\pm$ 0.07
La	L	13.09 $\pm$ 0.14	4.17 $\pm$ 0.05
Pr	L	35.53 $\pm$ 0.23	11.16 $\pm$ 0.07
(b)			
Element	Line	Mass%	Atom%
O	K	39.85 $\pm$ 0.10	78.63 $\pm$ 0.20
Fe	K	12.68 $\pm$ 0.07	7.17 $\pm$ 0.04
Co	K	1.36 $\pm$ 0.03	0.73 $\pm$ 0.02
Sr	L	22.48 $\pm$ 0.12	8.10 $\pm$ 0.04
La	L	23.63 $\pm$ 0.11	5.37 $\pm$ 0.03
(c)			
Element	Line	Mass%	Atom%
O	K	22.28 $\pm$ 0.19	35.83 $\pm$ 0.31
Ca	K	27.91 $\pm$ 0.21	30.22 $\pm$ 0.22
Fe	K	28.99 $\pm$ 0.29	22.53 $\pm$ 0.22
Co	K	2.23 $\pm$ 0.13	1.52 $\pm$ 0.09
La	L	15.99 $\pm$ 0.26	4.99 $\pm$ 0.08

A similar behavior was observed for the LCFC catalyst. The EDS quantitative analysis confirmed the presence of the expected La, Ca and Fe-rich matrix, while the elemental maps revealed localized Ca-rich domains. These observations are fully consistent with the XRD identification of residual calcium-containing secondary phases. Compared with ICP-MS, the EDS results suggest that the overall cationic composition is substantially preserved and that the slight deviations detected by ICP mainly arise from the averaging nature of the bulk analysis and from local compositional heterogeneities generated during crystallization.

For the PBC-HEO electrocatalyst, quantitative EDS confirmed the simultaneous presence of all the intended transition metals (Fe, Co, Ni, Cu and Zn) together with Pr and minor Ca, demonstrating the successful incorporation of the multicomponent cationic system into the oxide matrix. Although elemental mapping evidenced local Zn-rich regions and moderate compositional fluctuations, no severe depletion of the transition metals was observed. Interestingly, unlike ICP-MS, EDS did not indicate a significant loss of the alkaline-earth component, further supporting the hypothesis that the extremely low Ba concentration measured by ICP-MS is mainly attributable to matrix-dependent dissolution and recovery limitations rather than to the actual composition of the synthesized material.

Overall, the combined ICP-MS and SEM-EDS analyses provide complementary information on the chemical composition of the investigated electrocatalysts. Whereas ICP-MS offers an average bulk composition, SEM-EDS probes the local chemistry at the micrometer scale. The good agreement between the elemental maps, quantitative EDS analyses and structural characterization demonstrates that the co-precipitation route effectively preserves the target stoichiometry while revealing different degrees of local compositional heterogeneity, which become progressively pronounced from LSFC to LCFC and, particularly, to the compositionally complex PBC-HEO system. Nevertheless, the observed compositional heterogeneity is mainly local and occurs at the micrometer scale. Particularly, LSFC exhibits an almost homogeneous cation distribution, with only minor Sr-rich regions (the higher phase purity and crystallographic homogeneity observed for LSFC reduce the possible contribution of insulating secondary phases. However, electrical conductivity was not measured in the present investigation, and no direct conclusion concerning its magnitude or long-term stability can therefore be drawn), whereas LCFC contains localized Ca-rich domains associated with residual calcium-containing secondary phases. PBC-HEO shows the highest degree of heterogeneity, characterized by local enrichment of selected transition metals and moderate cation-concentration fluctuations, consistent with the presence of a minor Zn-rich secondary phase.

4. Conclusions

This work presented a comprehensive physicochemical characterization of three perovskite-based electrocatalysts synthesized via a simple co-precipitation route, namely two conventional lanthanum ferrites LSFC and LCFC and a compositionally complex oxide PBC-HEO, with the aim of evaluating their structural and microstructural features relevant for possible application as electrodes in reversible solid oxide cells (ReSOCs).

The combined DTA-TG and XRD analyses demonstrated that the three systems follow markedly different crystallization pathways, highlighting the strong influence of composition on phase evolution. While LSFC required high-temperature treatment (1400 °C) to achieve a single-phase perovskite structure, LCFC retained secondary calcium-containing phases even after prolonged calcination. In contrast, the compositionally complex PBC-HEO successfully crystallized at significantly lower temperatures (700 °C), although partial elemental segregation and secondary Zn-rich phases were observed upon further thermal treatment.

Vibrational spectroscopy further confirmed the successful formation of the targeted perovskitic oxide frameworks. Raman and FTIR analyses revealed progressively increasing lattice disorder from LSFC to LCFC and finally to PBC-HEO, consistent with the increasing compositional complexity of the investigated systems. In particular, the broad Raman features observed for PBC-HEO reflect the severe local lattice distortions induced by the random occupation of multiple transition-metal cations at the B-site while maintaining the overall perovskite structure.

The combined use of quantitative SEM-EDS and ICP-MS enabled a comprehensive assessment of the chemical composition at both local and bulk scales, demonstrating that the co-precipitation synthesis successfully preserved the intended cationic stoichiometry while revealing composition-dependent degrees of elemental homogeneity. These compositional findings, together with the structural and microstructural analyses, provide a robust basis for understanding the structure–composition relationships governing the investigated perovskite electrocatalysts and for guiding their future electrochemical optimization. Morphological investigation revealed markedly different particles and agglomerate architectures among the investigated materials. PBC-HEO exhibited the most open and interconnected network, whereas LSFC showed the highest crystallographic homogeneity and phase purity. These characteristics represent potentially relevant descriptors for electrode development, but their relationship with gas transport, electrical conductivity, oxygen-exchange kinetics and electrochemical activity cannot be established without dedicated quantitative measurements.

Overall, the results demonstrate that the adopted co-precipitation approach represents an effective and versatile route for preparing compositionally complex perovskite electrocatalysts with tailored structural characteristics. The comparison performed in this work highlights how composition strongly governs crystallization behavior, defect chemistry, phase stability and microstructure, providing valuable guidelines for the rational design of advanced oxide electrodes for high-temperature electrochemical devices.

Although the present work focused on the synthesis and physicochemical characterization of perovskite electrocatalyst powders, additional functional characterization remains necessary before their implementation in ReSOC devices. Future studies will address electrochemical performance, long-term redox stability, thermo-mechanical compatibility and durability under operating conditions, providing a comprehensive assessment of the most promising compositions.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app16157781/s1>.

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