Abstract: Protonic ceramic fuel cells (PCFCs) are promising electrochemical devices for the efficient and clean conversion of hydrogen and low hydrocarbons into electrical energy. Their intermediate operation temperature (500–800 °C) proffers advantages in terms of greater component compatibility, unnecessity of expensive noble metals for the electrocatalyst, and no dilution of the fuel electrode due to water formation. Nevertheless, the lower operating temperature, in comparison to classic solid oxide fuel cells, places significant demands on the cathode as the reaction kinetics are slower than those related to fuel oxidation in the anode or ion migration in the electrolyte. Cathode design and composition are therefore of crucial importance for the cell performance at low temperature. The different approaches that have been adopted for cathode materials research can be broadly classified into the categories of protonic–electronic conductors, oxide-ionic–electronic conductors, triple-conducting oxides, and composite electrodes composed of oxides from two of the other categories. Here, we review the relatively short history of PCFC cathode research, discussing trends, highlights, and recent progress. Current understanding of reaction mechanisms is also discussed.

Keywords: proton ceramic fuel cell; cathode; oxygen electrode; triple-conducting oxides; protonic-electronic conductor; composite

1. Introduction

The dependence of contemporary society on the combustion of fossil fuels for its energy requirements has created the urgent and overriding challenge of arresting the climate change that they promote by transitioning to a carbon-neutral, sustainable energy economy. Hydrogen is likely to play an expanding role as an energy vector in a sustainable and clean future economy, in which its chemical energy is converted to electrical energy in fuel cells [1]. Solid oxide fuel cells (SOFCs; commonly used abbreviations are listed in Table 1) based on oxide-ion conducting electrolytes have been intensely developed due to their high combined heat and power efficiency, long-term stability, low emissions, and relatively low cost [2,3]. The high operating temperature (typically in the range 800–1000 °C) provides the advantage of fuel flexibility, and their operation with simple hydrocarbons is often touted as a gateway to their widespread employment with hydrogen as fuel. Nevertheless, the high operating temperature is associated with long start-up times and problems with mechanical and chemical compatibility.

Consequently, there has been much research effort dedicated to lowering the operation temperature of SOFCs to better address small-scale applications (micro SOFCs and auxiliary power units) and reduce the costs associated with fabrication and operation [4]. In particular, a running temperature of 600 °C would allow the use of stainless-steel balance-of-plant components and cheaper interconnect materials. Moreover, the thermochemical efficiency of combustion of natural gas is maximum at this temperature [5].
Ceramic fuel cells with a proton-conducting electrolyte (protonic ceramic fuel cells, PCFCs, or proton-conducting solid oxide fuel cells, H\(^{+}\)-SOFCs) have been of ever-growing interest since the pioneering work of Iwahara starting in the 1980s on proton-conducting ceramic materials [6–9]. Such cells may also be operated in reverse to affect the electrolysis of water (protonic ceramic electrolysis cells, PCECs) [10,11]. These electrochemical cells may operate within an intermediate temperature (400–800 \(^\circ\)C), which is partly due to the higher mobility and lower activation energy of protons in comparison to oxide ions in this range. PCFCs have additional advantages: the water in the electrochemical reaction is generated in the cathode, so no further fuel recycling is required, and Ni in the fuel electrode remains at a suitably low oxygen partial pressure [5]. However, lowering the operating temperature creates much larger overpotentials at the electrode–electrolyte interface [12]. Specifically, the reaction kinetics related to oxygen reduction occurring in the air electrode are slower than fuel oxidation in the anode or ion migration in the electrolyte [13]. Hence, the cathode plays a major role in determining the efficiency of fuel-cell operation in the intermediate-temperature range. Electrochemical modelling has shown that, whereas lower ohmic resistance offered by thinner electrolytes is the easiest way to improve the performance of PCFCs, the performance is otherwise restricted by the attempted current density at the cathode, meaning that the cathode limits the performance of the whole cell [13].

A number of studies of protonic ceramic single cells, particularly earlier studies, employed a single metallic phase as an air electrode, most commonly platinum [5,14,15]. The elementary reaction steps occurring in a Pt cathode in contact with a protonic ceramic membrane in fuel-cell mode for the overall oxidation reaction have been described by Uchida et al. [16] as follows:

\[
2H^+ + \frac{1}{2}O_2 + 2e^- \rightarrow H_2O(g) \quad (1)
\]

\[
O_{2(g)} \rightarrow O_{2(ad)} \quad (2)
\]

\[
O_{2(ad)} \rightarrow 2O_{(ad)} \quad (3)
\]

\[
O_{(ad)} \rightarrow O_{(TPB)} \quad (4)
\]

\[
O_{(TPB)} + 2e^- \rightarrow O^2_{(TPB)} \quad (5)
\]

\[
O_{(TPB)}^2 + 2H^+ \rightarrow H_2O_{(TPB)} \quad (6)
\]

\[
H_2O_{(TPB)} \rightarrow H_2O(g) \quad (7)
\]

Analogous to the oxide-ionic conducting SOFCs, the cathodic, multistep reaction encompassed in Equations (2)–(7) may be considered as the “electrode surface path” [17]. It includes the diffusion of oxygen from the gas phase to adsorption (ad) on the electrode.

| Basic Concept | Abbreviation | Basic Concept | Abbreviation |
|---------------|--------------|---------------|--------------|
| Area Specific Resistance | ASR | Protonic Ceramic Fuel Cells | PCFCs |
| Distribution of Relaxation Times | DRT | Ruddlesden–Popper | RP |
| Electrode Polarization Resistance | \( R_p \) | Secondary Ion Mass Spectroscopy | SIMS |
| Electrochemical Impedance Spectroscopy | EIS | Solid Oxide Fuel Cells | SOFCs |
| Maximum Power Density | MPD | Thermogravimetric Analysis | TGA |
| Mixed Oxide-Ion Electron Conductors | MIECs | Triple Phase Boundary | TPB |
| Oxygen Reduction Reaction | ORR | Triple Protonic Oxide-Ionic Electron Hole Conducting Oxides | TCOs |
| Protonic Ceramic Electrolysis Cells | PCECs | | |
surface (2), oxygen dissociation at the surface (3), and diffusion to the triple phase boundary (TPB) (4), where protonic species from the electrolyte combine with the dissociated and reduced oxygen (5) to produce water (6), which is finally evaporated to the gas phase (7).

The issue of cathode design, replacing platinum with oxides, has been addressed with different approaches. Then, the oxidation reaction is necessarily more complex than the scheme above. These strategies include:

(i) Improving the electronic conductivity in proton-conducting oxides via substitution of mixed-valence cations (Figure 1a).

(ii) Incorporation of a mixed oxide-ion–electronic conductor (MIEC) analogous to the classical oxide-ion conducting SOFC cathode (Figure 1b).

(iii) Employing so-called triple-conducting oxides (TCOs) with proton, oxide-ion, and electron conductivity (Figure 1c).

(iv) Designing composite electrodes with a proton-conducting oxide (including improving electron conductivity via strategy (i) and an oxide-ion and electron-conducting component (Figure 1d).

Figure 1. Electrochemical reaction steps corresponding to the cathodic reduction reaction occurring through: (a) the “electrode-surface path” (1) and “bulk-electrode path for protons” (2) for a mixed protonic–electronic conductor; (b) the “electrode-surface path” (1) and “bulk-electrode path for oxide ions” (2) for a mixed oxide-ionic–electronic conducting electrode; (c) the “electrode-surface path” (1), “bulk-electrode path for protons”, (2) and “bulk-electrode path for oxide ions” (3) for a triple protonic-oxide-ionic–electronic conducting oxide; (d) “bulk-electrode path for oxide ions” (1), “bulk-electrode path for protons” (2) and (3), for a composite based on an oxide ionic–electronic conductor and a mixed protonic–electronic conductor.
There is inevitably a certain degree of overlap among these categories. Depending on conditions of temperature and atmosphere, many proton-conducting oxides also exhibit electron-hole or oxide-ion conductivity. Hence, materials categorized as mixed protonic–electronic conductors may, under certain conditions, be triple oxide-ion proton electron-hole conductors, which is a subject of much current interest in the design of cathodes for PCFCs. Similarly, materials designated as triple conductors are not expected to exhibit transport by all three species over a wide range of conditions. It should be noted that the contributions of the different charge carriers in a given material are generally not well established, requiring detailed study. Moreover, modelling of the performance of PCFCs is considerably more complex than is the case for SOFCs due to the mixed-conducting nature (i.e., oxide ions, protons, and electron holes) of the electrolyte. Previous studies indicate that the electrolyte membrane contributes the major polarisation loss and that thinner electrolytes with better ionic conductivity should be used [18]. The concentration of polarisation associated with steam transport may be lowered by reducing the cathode thickness and enlarging the pore space, although the cathode should be thicker than the effective charge-transfer region (20–50 µm).

The importance of the cathode in the development of PCFCs has only been given more prominence in the past few years. Nevertheless, considerable progress has been achieved in this time, warranting a review of developments and an overview of the current state-of-the-art in the field. Here, we provide a perspective on the status of oxide cathodes for protonic ceramic fuel cells, adopting the broad categorization listed above to classify the types of material that have been studied to date.

2. Mixed Proton–Electron-Conducting Cathodes

The introduction of a mixed proton–electron conductor (PEC) as air electrode extends the electrochemical reaction from the triple-phase boundaries at the cathode–electrolyte interface to the whole electrode surface. Thus, the model for Pt may be extended to include H\(^+\) migration from the H\(^+\)-conducting electrolyte through the cathode and over the cathode surface to the reaction sites (Figure 1a) [19], assuming that oxide-ion transport is negligible in the cathode material. This approach involves a new electrochemical path for the cathodic reaction, which may coexist in parallel with the “electrode surface path”, and is addressed as “bulk electrode path for protons”. This multistep reaction path may be schematized as follows:

\[
\begin{align*}
O_2(g) & \rightarrow O_2(ad) \quad (8) \\
O_2(ad) & \rightarrow 2O(ad) \quad (9) \\
O(ad) + 2e^- & \rightarrow O^{2-}(ad) \quad (10) \\
2H^+(\text{electrolyte}) & \rightarrow 2H^+(\text{bulk–electrode}) \quad (11) \\
2H^+(\text{bulk–electrode}) & \rightarrow 2H^+(as) \quad (12) \\
2H^+(as) + O^{2-}(ad) & \rightarrow H_2O(ad) \quad (13) \\
H_2O(ad) & \rightarrow H_2O(g) \quad (14)
\end{align*}
\]

According to the electrochemical steps described by Equations (8)–(14), oxygen gas is diffused, adsorbed, dissociated, and reduced, as it occurs in the “surface electrode path” (Equations (8)–(10)). In contrast, the protonic species are transferred from the electrolyte to the cathode component (Equation (11)) and diffuse through the electrode bulk (Equation (12)) to the active sites (H\(^+\)\(_{\text{as}}\) in Equation (12)), corresponding to the whole surface of the electrode, where the reaction with the adsorbed oxide ions produces water (13), which is then desorbed from the surface to the gas phase (14).
The diffusion of protonic species toward the reaction sites on the electrode component may occur through the electrode bulk (Equation (12)) and/or through the electrode surface, according to:

$$2H_{\text{surface}}^+ \rightarrow 2H_{(a)}^+.$$  (15)

High electronic conductivity is required in the cathode compartment not only for the reaction reaction (Equation (10)) but also so that current flow around the cell is as uninhibited as possible.

Several studies have been performed with the aim of increasing the electronic conductivity of proton-conducting oxides. One of the earliest attempts by Mukundan et al. [20], dating back to 1996, involved doping the BaCe$_{0.8}$Y$_{0.2}$O$_{3-\delta}$ (BCY20; abbreviations of commonly used compositions are listed in Table 2) proton conductor with praseodymium on the perovskite B-site. Greater Pr content in the BaCe$_{0.8}$Pr$_{0.2}$O$_{3-\delta}$ solid solution increases electron-hole conductivity, and a cathodic overpotential resistance of 0.47 Ω·cm$^2$ is reported at 800 °C for BaPr$_{0.8}$Gd$_{0.2}$O$_{2.9}$ [21]. Praseodymium has proved to be a popular dopant for enhancing mixed conductivity in proton-conducting perovskites, since mixed Pr$^{3+}$ and Pr$^{4+}$ valence states generate considerable electron-hole transport. Consequently, the high Pr contents in Ba(Pr,R)O$_{3-\delta}$ (R = Zr, Ce) phases are associated with predominant electron conductivity; however, proton conductivity diminishes with Pr content, and stability in wet and dry reducing conditions, wet oxidizing conditions, and CO$_2$-containing atmospheres is dramatically poorer [22–24]. Nevertheless, a stable power output is reported for a BaPr$_{0.8}$In$_{0.2}$O$_{3-\delta}$ cathode with a peak power density of 0.688 W·cm$^{-2}$ at 750 °C on a BaCe$_{0.5}$Zr$_{0.1}$Y$_{0.1}$Yb$_{0.1}$O$_{3-\delta}$ (BCZYb7111) electrolyte [25].

### Table 2.
Abbreviations used in the text corresponding to selected, frequently employed compositions.

| Composition | Abbreviation | Composition | Abbreviation |
|-------------|--------------|-------------|--------------|
| BaCe$_{0.8}$Gd$_{0.2}$O$_{3-\delta}$ | BCG20 | Ce$_{0.5}$La$_{0.5}$O$_{1.75}$ | 50LDC |
| BaCe$_{0.8}$Sm$_{0.2}$O$_{3-\delta}$ | BCS20 | Ce$_{0.8}$Sm$_{0.2}$O$_{2.8}$ | 20SDC |
| BaCe$_{0.8}$Y$_{0.2}$O$_{3-\delta}$ | BCS10 | GdBaCo$_2$O$_{5+4}$ | GBCO |
| BaCe$_{0.8}$Ba$_{0.2}$O$_{3-\delta}$ | BCY20 | LaCoO$_{3-\delta}$ | LCO |
| BaCe$_{0.5}$Y$_{0.15}$O$_{3-\delta}$ | BCY15 | LaFeO$_3$ | LF |
| BaCe$_{0.9}$Y$_{0.1}$O$_{3-\delta}$ | BCY10 | La$_3$NiO$_{4+\delta}$ | LNO |
| BaCe$_{0.9}$Y$_{0.1}$O$_{3-\delta}$ | BCYb10 | LaNi$_{0.7}$Fe$_{0.4}$O$_{3-\delta}$ | LNF |
| BaCe$_{0.9}$Zr$_{0.1}$O$_{3-\delta}$ | BCZY27 | La$_{0.7}$Sr$_{0.3}$FeO$_{3-\delta}$ | LSC55 |
| BaCe$_{0.9}$Y$_{0.1}$O$_{3-\delta}$ | BCZY44 | La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ | LSC64 |
| BaCe$_{0.5}$Zr$_{0.2}$Y$_{0.5}$O$_{3-\delta}$ | BCZY53 | La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ | LSCF |
| BaCe$_{0.5}$Zr$_{0.2}$Y$_{0.5}$O$_{3-\delta}$ | BCZY62 | La$_{0.7}$Sr$_{0.3}$Co$_{0.2}$Fe$_{0.5}$O$_{3-\delta}$ | LSCM |
| BaCe$_{0.5}$Zr$_{0.2}$Y$_{0.5}$O$_{3-\delta}$ | BCZY71 | La$_{0.7}$Sr$_{0.3}$FeO$_{3-\delta}$ | LSF73 |
| BaCe$_{0.8}$Zr$_{0.1}$Y$_{0.1}$O$_{3-\delta}$ | BCZY81 | La$_{0.8}$Sr$_{0.2}$FeO$_{3-\delta}$ | LSF82 |
| BaCe$_{0.5}$Zr$_{0.4}$Y$_{0.1}$Yb$_{0.1}$O$_{3-\delta}$ | BCZYb4411 | La$_{0.5}$Sr$_{0.5}$MnO$_{4-\delta}$ | LSM55 |
| BaCe$_{0.7}$Zr$_{0.3}$Y$_{0.1}$Yb$_{0.1}$O$_{3-\delta}$ | BCZYb7111 | La$_{0.7}$Sr$_{0.3}$MnO$_{3-\delta}$ | LSM73 |
| BaCe$_{0.5}$Sr$_{0.5}$Fe$_{0.5}$O$_{2-\delta}$ | BSCF | La$_{0.5}$Sr$_{0.5}$MnO$_{4-\delta}$ | LSF82 |
| BaZr$_{0.3}$O$_{3-\delta}$ | BZO | NdBa$_{0.5}$Sr$_{0.5}$Co$_{1.0}$Fe$_{0.5}$O$_{4+\delta}$ | NSCF |
| BaZr$_{0.3}$Y$_{0.2}$O$_{3-\delta}$ | BZY20 | PrBaCo$_2$O$_{5+\delta}$ | PBBO |
| BaZr$_{0.5}$Y$_{0.15}$O$_{3-\delta}$ | BZY15 | PrBa$_{0.5}$Sr$_{0.5}$Co$_{1.5}$Fe$_{0.5}$O$_{5+\delta}$ | PBSCF |
| BaZr$_{0.9}$Y$_{0.1}$O$_{3-\delta}$ | BZY10 | Sm$_{0.5}$Sr$_{0.5}$FeO$_{3-\delta}$ | SSF |
| Ce$_{0.9}$Gd$_{0.1}$Y$_{0.1}$O$_{2-\delta}$ | 10GDC | Sm$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ | SSC |

For BaZrO$_3$-based phases, co-doping strategies involving solid solutions, such as BaZr$_{0.8}$Pr$_{0.2}$Y$_{0.2}$O$_{3-\delta}$ [26] and BaZr$_{0.9}$Pr$_{0.1}$Gd$_{0.1}$O$_{3-\delta}$ [27], have been employed, and both have good chemical stability and mixed conductivity are achieved when a high Zr content is maintained. Heras-Juaristi et al. reported the formation of complete solid solutions between the important electrolyte composition BaZr$_{0.7}$Ce$_{0.2}$Y$_{0.1}$O$_{3-\delta}$ and BaPr$_{0.9}$Y$_{0.1}$O$_{3-\delta}$ [28,29], indicating that although the total conductivity of the solid-solution members may be insufficient for a good electrode performance (0.4 S·cm$^{-1}$ for BaZr$_{0.175}$Ce$_{0.05}$Pr$_{0.675}$Y$_{0.1}$O$_{3-\delta}$...
at 900 °C in oxidizing conditions), such Pr-doped phases with mixed conductivity may be employed in a composite cathode together with a highly conducting phase.

The mixed valence states of Fe and Co may also be exploited to enhance electronic conductivity in proton-conducting perovskite oxides [30,31]. Wu et al. [32] recently investigated Fe-substituted BaZr0.8Y0.2O3−δ (BZY20) as cathode material, reporting an electrode polarisation resistance (R_p) of 0.28 Ω·cm² and a peak power density of 0.322 W·cm⁻² at 700 °C for the composition BaZr0.2Fe0.6Y0.2O3−δ (Figure 2).

![Figure 2](image)

**Figure 2.** Microstructure of a BaZr_{0.8-x}Fe_{x}O_{3−δ} (x = 0.6) cathode over a BaCe_{0.7}Zr_{0.1}O_{3−δ} electrolyte in an anode-supported cell (a); Arrhenius dependence of the electrode polarisation resistance for different Fe contents in the BaZr_{0.8-x}Fe_{x}O_{3−δ} series (b); current–voltage curves and current–power density curves for single cells with BaZr_{0.2}Fe_{0.6}O_{3−δ} (c) and BaFe_{0.8}O_{3−δ} cathodes (d). Copyright 2020 by Elsevier [32].

Fe doping in the BaCe_{0.7-x}Zr_{0.2}Y_{0.1}Fe_{x}O_{3−δ} series is reported to enhance transport properties (R_p = 0.21 Ω·cm² at 700 °C), but thermal expansion also increases substantially with increasing Fe content [33]. Cobalt is documented to have a moderate solid-solution limit in the series BaZr_{1−x}Co_xO_{3−δ} but a promising electrode polarisation of 0.19 Ω·cm² at 700 °C was achieved for the x = 0.4 composition [31]. Other attempts at doping proton conductors for cathode applications include substituting Ce with mixed-valence Bi in the series BaCe_{1−x}Bi_xO_{3−δ} (0 ≤ x ≤ 0.5), which enhances total and electron conductivities but decreases proton conductivity [34].

Strategies other than cation doping have generally been employed for the development of cathodes for cells based on the LaNbO_4 scheelite-type proton conductor [35]. However, Solis and Serra observed enhanced p-type transport on doping the La site with Pr, suggesting that the Pr-doped material may form the basis of a composite cathode [36].
With the exception of some noted examples, it is generally the case that the doping of proton-conducting oxides to enhance mixed conductivity has not been met with broad success due to the limited electronic or protonic conductivity of the doped materials, limited solid-solution ranges for the doped materials, and stability issues for high dopant concentrations. Nevertheless, there is much scope for the greater employment of proton-conducting phases, which are doped to enhance the electronic component of composite cathodes [29,36].

3. Mixed Oxide-Ion–Electron-Conducting Cathodes

A more widely employed strategy is to adopt mixed oxide-ion/electron-hole conductors (MIECs) as air electrode for the proton-conducting electrolyte. Oxygen may then be adsorbed on the cathode surface, which is followed by dissociation and migration as oxide ions (Equations (8)–(10)) either on the surface (“electrode surface path”) or through the cathode bulk (“bulk-electrode path for oxide ions”). However, the reaction sites are limited to the triple-phase boundaries on the electrolyte surface, where the diffused oxide ions meet protons (Figure 1b). The “electrode surface path” in these components is described by Equations (2)–(7), whereas the “bulk-electrode path for oxide ions” is described as follows:

\[
\begin{align*}
O_2(g) &\rightarrow O_2(ad) \quad (16) \\
O_2(ad) &\rightarrow 2O(ad) \quad (17) \\
O(ad) + 2e^- &\rightarrow O^{2-}_\text{bulk} \quad (18) \\
O^{2-}_\text{bulk} &\rightarrow O^{2-}_\text{TPB} \quad (19) \\
O^{2-}_\text{TPB} + 2H^+ &\rightarrow H_2O_{\text{TPB}} \quad (20) \\
H_2O_{\text{TPB}} &\rightarrow H_2O(g). \quad (21)
\end{align*}
\]

Since the 1990s, there has been a general trend in SOFC research to replace Mn in the B site of the classical LaMnO$_3$-based perovskite cathode with Co and/or Fe [37]. The higher diffusion of oxide ions and faster kinetics at the electrode/electrolyte interface than LaMnO$_3$-based air electrodes make the Co/Fe-containing perovskites more favorable in the lower-temperature range where their higher thermal expansion is less problematic. Hence, the first studies involving cathodes for H$^+$-conducting solid oxide cells frequently employed perovskites with Fe and/or Co-containing B-site cations. Nevertheless, Wang et al. recently demonstrated a high uptake of protons in La$_{0.7}$Sr$_{0.3}$MnO$_3$–δ by using XAFS, TG, and hydration experiments [38].

One of the first documented attempts to replace Pt as the cathode in laboratory single cells was made by Iwahara et al. [39], who experimented with a limited number of nickelate, manganite, and cobaltate cathodes, finding the best performance for La$_{0.6}$Ba$_{0.4}$CoO$_3$–δ (0.18 W·cm$^{-2}$ at 1000 °C). Perovskites with Co as the principal B-site cation generally provide high power outputs. A competitive single-cell performance of 0.3 W·cm$^{-2}$ at 700 °C was reported in 2008 with the classical SOFC cathode La$_{0.5}$Sr$_{0.5}$CoO$_3$–δ on BaCe$_{0.7}$Zr$_{0.1}$Y$_{0.2}$O$_3$–δ (BCZY71) electrolyte [40]. The performance of SrCo$_{0.9}$Sb$_{0.1}$O$_3$–δ, which was previously reported as a good SOFC cathode [41], compared favourably to La$_{0.9}$Sr$_{0.1}$MnO$_3$–δ (LSM82), achieving an output of 0.259 W·cm$^{-2}$ at 700 °C on BCZY71 [42]. It was shown that Sm$_{0.5}$Sr$_{0.5}$CoO$_3$–δ (SSC) prepared by planetary bead-milling had improved performance over the material without such treatment, highlighting the importance of microstructure on electrode performance [43]. Similarly, an improvement in the performance of SrCo$_{0.9}$Nb$_{0.1}$O$_3$–δ is documented by the wet chemical method in comparison to solid-state reaction (0.348 W·cm$^{-2}$ and 0.204 W·cm$^{-2}$, respectively, at 700 °C) [44]. Cobaltites have also achieved good performances as air electrodes in protonic ceramic electrolysis cells (PCECs), with a cell composed of an anode of Ba$_{0.5}$La$_{0.5}$CoO$_3$–δ
and an electrolyte of Ba(Zr0.5Ce0.4)8/9Y2O3−δ, reaching a hydrogen evolution rate of 127 mol·cm−2·min−1 at 0.5 A·cm−2 and 600 °C [45].

Other authors have focused on Fe/Co-containing perovskites that are well known as SOFC cathodes, particularly La0.6Sr0.4Co0.2Fe0.8O3−δ (LSCF). Meng et al. [46] achieved a power density of 0.753 W·cm−2 at 700 °C with LSCF on a BaCe0.95Tb0.05O3−δ electrolyte. In one of the first reports of tubular PCFCs, LSCF electrodes were employed in anode-supported cells on BCZY71 electrolyte with a power range of 0.079–0.189 W·cm−2 in the temperature range 700–850 °C [47]. In terms of single-cell experiments, a much improved performance was found with nanostructured LSCF cathode, again prepared by planetary bead-milling, in comparison to the unmilled LSCF phase [48]. An alternative strategy to improve the performance of LSCF involves the infiltration of BaCO3 nanoparticles forming a synergetic catalyst, which reduced the polarisation resistance by nearly 75% from 1.123 to 0.293 Ω·cm2 at 700 °C, yielding a power density of 0.404 W·cm−2 [49].

The well-known SOFC cathode Ba0.5Sr0.5Co0.8Fe0.2O3−δ (BSCF) has also regularly been used and compared as a PCFC air electrode [50–52]. A very high power density of up to 0.800 W·cm−2 at 700 °C, and a stable performance in CO2, with BaZr0.4Ce0.45Y0.15O3−δ as the electrolyte has been reported (Figure 3) [53].

Dailly et al. compared the performance of BSCF, LSCF, and Pr2NiO4−δ (a phase that is discussed further in the next section), reporting that the area-specific resistance (ASR) values of the electrode process were similar but that, at low temperature, BSCF appeared to be the most efficient of the three cathodes on BaCe0.9Y0.1O3−δ (BCY10) electrolyte [51].

However, BSCF is reported to react with the LaNbO4-based electrolyte, whereas La0.75Sr0.25Cr0.5Mn0.5O3−δ (LSCM) is chemically compatible with a lower ASR value for the electrode process [54]. Similar behavior was observed with the proton-conducting electrolyte La6WO12, which is stable with La0.5Sr0.5MnO3−δ (LSM73) and LSCM but reacts with BSCF [55]. In 2013, Shang et al. [56] documented that the phase BaCo0.4Fe0.4Zr0.2O3−δ (BCFZ) exhibits lower polarisation resistance, longer performance stability, and better compatibility with the BCZYYb7111 electrolyte than LSCF under the same conditions, achieving a power density of 0.225 W·cm−2 at 600 °C. Rare-earth doping in the related BaCo0.4Fe0.55Ce0.1Re0.3O3−δ (Re = Y, Gd; x = 0.1) system has also been reported, with the Gd-doped phase exhibiting a promising peak power density of 0.504 W·cm−2 at 600 °C in a cell with BCZYYb7111 as the electrolyte [57].

Tolchard et al. [58] assessed the reactivity of SOFC perovskite cathodes LaMO3 (M = Mn, Fe, Co) and the layered phase La0.6Sr0.4NiO4+δ (x = 0, 0.8) in contact with SrCeO3-based electrolyte, indicating that the reaction occurs readily on high-temperature sintering for the perovskite compositions due to Sr diffusion from the electrolyte to the cathode; however, the Ruddlesden–Popper-type oxide La1.2Sr0.8NiO4+δ does not react. The chemical compatibility of the same perovskite compositions with BaZrO3-based electrolytes was better, with only minor interdiffusion of Ba and La occurring [59]. Nevertheless, the authors

Figure 3. Microstructure of BSCF cathode on BZCY40 electrolyte (a), single-cell performance (b), and the corresponding Nyquist spectra at different water partial pressures (c). Copyright 2016 by Elsevier [53].
point out that thermal expansion mismatch should be controlled with careful choice of chemical substitutions.

The significant, deleterious effects of cobalt on stability in H2O and thermal expansion, as well as its limited availability and increasing cost due to greater use, have promoted the study of alternative Co-free materials. (La, Sr)FeO3−δ has proved to be a popular choice as a Co-free cathode since Yamaura et al. [60] showed that the overpotential of La0.7Sr0.3FeO3−δ was smaller than that of both La0.7Sr0.3MnO3−δ and La0.7Sr0.3CoO3−δ using SrCe0.95Yb0.05O3−δ as the electrolyte. Yuan et al. reported a power output of 0.538 W cm−2 at 650 °C on BCZY71 electrolyte using cobalt-free SrFe0.95Nb0.05O3−δ as the cathode [61]. A further La-free electrode with good performance is Ba0.5Sr0.5Fe0.8Zr0.2O3−δ [62], with a power output of 0.486 W cm−2 at 700 °C on BCZY71 electrolyte.

Nevertheless, the general tendency is for electrode performance to improve with the inclusion of Co in the cathode composition. A study of the substitution of Fe on the B-site in the series Nd0.5Ba0.5Fe0.9M0.1O3−δ (M = Ni, Cu, Co) indicates that the introduction of cobalt leads to higher ionic conductivity and lower polarisation resistance [63].

The RBa(Co,M)4O7 series (R = Y, Ca; M = Zn, Fe, Al) with tetrahedral corner-sharing (Co/M)O4 units has also been studied as both the SOFC and PCFC cathode for exhibiting a high catalytic activity and low thermal-expansion coefficient compatible with typical electrolyte materials; the Zn-containing composition YBa2Co3ZnO7 is most promising due to its high thermal stability [64]. Y0.8Ca0.2BaCo4O7 exhibits a good electrochemical performance on BCZY71 electrolyte, achieving a maximum power density (MPD) of 0.472 W cm−2 at 700 °C [65]. The same composition was deposited by a tape-calendering method on BaCe0.5Zr0.5Y0.2O3−δ (BCZY53) electrolyte, providing an MPD of 0.308 W cm−2 at 725 °C [66].

Other cobaltite materials with layered misfit-type structures, consisting of alternating layers of a disordered AO-CoO-AO rock-salt-type layer and a Co-O CdI2-type layer stacked along the c-direction, have been of interest due to their good thermoelectric properties [67]. The Ca3−xLa2xCo4O9+δ (x = 0, 0.3) series was reported to have high electrical conductivity (53 S cm−1 at 600 °C, for x = 0.3) and promising electrocatalytic activity on BCY10 electrolyte [68]. The composition Ca3Co4O9+δ was employed more recently in a reversible protonic ceramic cell based on a BCZY53 electrolyte, yielding a power density of ≈0.290 W cm−2 in fuel-cell mode and an electrolysis current of ≈0.580 A cm−2 at 700 °C [69].

4. Triple Proton Oxide Ion Electron Hole-Conducting Oxides

It has been well known for some time that in certain oxides, the transport species protons, oxide ions, and electrons (electron holes in oxidising conditions) may exist simultaneously. The advantage of triple-conducting oxides (TCOs) as electrode materials for the oxygen reduction reaction in PCFCs is that both protons from the electrolyte and oxide ions adsorbed from the air may migrate through the bulk and over the surface of the cathode, extending the reaction area over the whole of the electrode. In this situation, the cathodic electrochemical reaction encompasses the parallel contributions from the “electrode-surface path”, “bulk-electrode path for protons”, and “bulk-electrode path for oxide ions” according to Equations (2)–(21), as shown in Figure 1c.

Some of the most prominent triple-conducting oxides forming the basis of study for PCFC cathodes are layered perovskites, which fall into the class of either double perovskites AB2O4±δ [70] or Ruddlesden–Popper (RP) perovskite-related structures of general formula A(m+1)BnO3m+n−1 [71]. Initial reports of such phases in the context of proton-conducting cells focus on compositions employed in oxide-ion-conducting electrolyte SOFC research as mixed oxide-ionic–electronic conductors, and they do not necessarily involve or consider three conducting species in the electrochemical oxidation reaction. Determination of the relations of proton, oxide-ion, and electron-hole partial conductivities requires detailed experiments, such as the concentration-cell method [72] or measurements in different oxygen and water-vapor partial pressures, followed by analysis based on defect-
chemistry relations [73–75]. Generally, these experiments are only successfully employed for a significant proton contribution, and partial-conductivity data are not available for the great majority of candidate materials. Instead, hydration experiments coupled with thermogravimetric analysis (TGA) have been used to indicate the triple-conducting nature of materials with potential as PCFC cathodes.

In one of the first reports of layered perovskites as PCFC cathode, published in 2009, Fontaine et al. adopted different architectures (CaTi0.5Fe0.1O3−δ), and the RP series La2NiO4+δ and La4Ni3O10) as electrodes for LaNbO4-based electrolyte thin films [76]. The layered RP-type cathode was then employed on BCY10 electrolyte, providing a power density of 0.130 W cm−2 at 650 °C [77]. Dailly et al. [78] studied a series of perovskite oxides AMO3−δ (A = La, Ba; Sr; M = Mn, Fe, Co, Ni) and layered RP-type materials A2MO4+δ (A = La, Nd, Pr or Sr; M = Ni), noting that the lowest electrode polariation resistances are observed for Ba0.8Sr0.2Fe0.8Co0.2O3−δ and Pr2NiO4+δ. Dailly and Marrony then reported the successful operation of a single cell over 1000 h with an Nd2NiO4 layered cathode, although the power output was low (0.060 W cm−2 at 600 °C) [79].

The first papers to explicitly associate the layered perovskites with triple-conducting behavior appeared in 2012 [80,81]. Grimaud et al. [80] investigated the hydration and electrochemical properties of LSFC, BSCF, PrBaCo2O5+δ (PBCO) and La2NiO4+δ by TGA and polarisation studies, indicating that proton transfer and water release appear to be the rate-determining steps for BSCF, PBCO, and Pr2NiO4+δ, but that no rate-determining step involving protons was found for LSFC. The same group also studied the effect of Sr content in the Pr2−xSr1+xNiO4+δ system on the oxygen reduction reaction and hydration, indicating that evidence for triple conduction exists in the Pr2NiO4+δ phase but not in the Sr-doped composition [81].

Ruddlesden–Popper nickelates of the form A2NiO4+δ, and in particular the praseodymium analogue (Pr2NiO4+δ), have continued to be the focus of study in protonic ceramic cells. A high performance of 0.82 W cm−2 was recently obtained with a Pr2NiO4+δ cathode on BaCe0.5Zr0.3Y0.2O3−δ electrolyte at 650 °C, employing a microwave heat treatment to minimize the reaction between the cathode and electrolyte [82]. In electrolysis mode, a Pr1.95Ba0.05NiO4+δ oxygen electrode was reported to provide an excellent hydrogen production rate of 19 mL min−1 at 600 °C on a tubular BaCe0.2Zr0.3Dy0.2O3−δ electrolyte [83]. Ba-doping in the nickelate series Nd2−xBa2NiO4+δ is documented to reduce diffusion of Ba from the electrolyte to the electrode [84], whereas anion doping with F in the series Nd1.9Ba0.1NiO4+δFy improves the electrochemical performance in electrolysis mode [85]. A single cell with La1.2Sr0.8Ni0.6Fe0.4O4+δ (LSNF) cathode based on a BCZY71 electrolyte achieved a maximum power density of 0.781 W cm−2 with a low interfacial polarisation resistance of 0.078 Ω cm2 at 700 °C, demonstrating high long-term stability [86]. Another elevated power output was recently reported for Ca-doped La2NiO4, with a composition of La1.5Ca0.5NiO4+δ, offering an MPD of 0.923 W cm−2 at 700 °C [87]. The effect of Co-doping in RP-type cathodes based on La3Ni2O7 is explored by Chen et al. [88], who indicate that Co on the Ni site improves activity toward the oxygen reduction reaction. In contrast to general trends, the substitution of Co for Fe in the LaSrCo1−xFe1+xO4+δ RP-type series was found to improve electrochemical performance [89]. The influence of the microstructure on the performance of RP-based cathodes has also been investigated. Nanofibers of La2NiO4 and LaNi0.6Fe0.4O3−δ were obtained by an electrospinning technique and employed as a highly efficient cathode, reaching a power density of 0.551 W cm−2 at 700 °C [90].

An interesting nickelate with a different layered structure, in which lithiation is reported to improve conductivity and cathode activity in SOFCs, is Li0.2Ni0.79Co0.2Zn0.01O2 [91]. Fan and Su [92] explored the electrode properties of an LiNi0.8Co0.2O2 cathode on BCZY71 electrolyte, which rendered an MPD of 0.410 W cm−2 at 650 °C; TGA and electrochemical impedance spectroscopy (EIS) were employed to indicate the triple-conducting nature of the material in wet conditions. An improved electrode performance with increasing water content indicated a role of protons in BSCF as well as Pr2NiO4+δ [93].
The first reports of using double perovskites in protonic ceramic cells appear around the same period as the RP nickelate phases. In 2008, GdBaCo$_2$O$_{5+\delta}$ (GBCO) was employed on a BCZY71 electrolyte, reaching a power density of 0.266 W·cm$^{-2}$ at 700 °C [94]. The same authors subsequently achieved better performances of 0.382 and 0.533 W·cm$^{-2}$ at 700 °C on substituting Gd with Sm (SmBaCo$_2$O$_{5+\delta}$) [95] and then also partially substituting Ba with Sr (SmBa$_{0.5}$Sr$_{0.5}$Co$_2$O$_{5+\delta}$) [96], respectively. Early studies of double perovskites include that of Ling et al. [97], who compared the performance of LaBaCuMO$_{5+\delta}$ (M = Fe, Co) and similarly found that the better single-cell performance of the Co-containing phase (0.432 W·cm$^{-2}$ at 700 °C), in comparison to the Fe-containing analogue (0.327 W·cm$^{-2}$ at 700 °C), was attributable to the higher catalytic activity of the former.

The term “triple-conducting oxide” comes to greater prominence soon after the studies of Grimaud et al. [80,81] when Kim et al. reported an excellent power output of 1.61 W·cm$^{-2}$ at 750 °C for a single cell with a BCZYb7111 electrolyte and the layered double-perovskite cathode NdBa$_{0.5}$Sr$_{0.5}$Co$_{0.5}$Fe$_{0.5}$O$_{5+\delta}$ (NBSCF) [98]. Strandbakke et al. [99] studied a series of double perovskites BaGd$_{0.8}$La$_{0.2}$Co$_2$O$_{5+\delta}$, BaGdCo$_{1.5}$Fe$_{0.5}$O$_{5+\delta}$, PrBaCo$_2$O$_{5+\delta}$, and BaPrCo$_{1.4}$Fe$_{0.6}$O$_{5+\delta}$ on BCZY71 electrolyte, observing that polarisation resistances were lowest for the Fe-free materials. The electrode impedance responses were composed of two apparent contributions, which were attributed to charge transfer and diffusion or surface-related processes, and they were modeled with a system of two ionic and one electronic charge carriers [99]. Brieuc et al. [100] employed molecular dynamics to study proton diffusion in GBCO and found that the predominant mechanism was proton transfer between neighbouring oxygens (Grötthuss mechanism) but that vehicular migration via OH groups may also occur.

The praseodymium-containing analogue of NBSCF, PrBa$_{0.5}$Sr$_{0.5}$Co$_{1.5}$Fe$_{0.5}$O$_{5+\delta}$ (PBSCF), was subsequently reported to proffer an exceptional power density (0.500 W·cm$^{-2}$ at 500 °C) when employed as a dense interlayer between the electrolyte BaZr$_{0.4}$Sc$_{0.6}$O$_{2+\delta}$ and a cathode of the same material [101]. The same group then demonstrated reversible operation of the NiO-BCZYb4411/BCZYb4411/PBSCF cell, which showed negligible degradation after 500 h of operation at 550 °C with a current density of −1.80 A·cm$^{-2}$ at 600 °C at an operating voltage of 1.3 V (Figure 4) [102]. PBSCF has recently been employed as a cathode in a thin film PCFC in which each of the active components (anode functional layer, electrolyte, and cathode) was fabricated by a slurry spin-coating technique on a BaCe$_{0.6}$Zr$_{0.2}$Y$_{0.1}$Yb$_{0.1}$O$_{2-\delta}$ anode support, reaching an MPD of 0.250–0.650 W·cm$^{-2}$ at 500–600 °C [103].

The role of the effect of A-site cation ordering on the cathode performance and chemical stability in double perovskites is investigated for a-site cation-ordered LaBaCo$_2$O$_{5+\delta}$ and -disordered La$_{0.5}$Ba$_{0.5}$CoO$_{2-\delta}$ by Bernuy-López et al. [104], observing that A-site cation ordering leads to a higher oxygen-vacancy concentration, which explains the better electrochemical performance of LaBaCo$_2$O$_{5+\delta}$ compared to the disordered phase. An A-site-deficient, layered perovskite, (PrBa$_{0.8}$Ca$_{0.2}$)$_{0.95}$Co$_2$O$_{5-\delta}$, was developed as an oxygen electrode for a reversible protonic ceramic cell where current density reached −0.72 A·cm$^{-2}$ at 1.3 V, and a peak power density of 0.540 W·cm$^{-2}$ was obtained at 600 °C in electrolysis and fuel-cell mode, respectively, which were much higher values than the A-site stoichiometric analogue [105]. A-site deficiency is generally recognized to improve the chemical stability of perovskite oxides and may also increase the oxide-ion-vacancy concentration and thereby the electrochemical performance.

Zhou et al. [106] have recently developed a double perovskite cathode, Sr$_2$Sc$_{0.1}$Nb$_{0.1}$Co$_{1.5}$Fe$_{0.5}$O$_{2-\delta}$ (SSNCF), for a dual ion (oxide-ion and proton) SOFC, where triple conduction in the cathode is reported to lead to an enhanced electrochemical performance, 0.840 W·cm$^{-2}$ at 650 °C on BCZYb7111 electrolyte. The authors employed an oxide-ion blocking technique in combination with H$_2$ and O$_2$ permeability measurements to demonstrate proton and oxide-ion transport. Another report of high performance with a double-perovskite
cathode concerns GdBaCuCoO$_{5+\delta}$ on a BCZY71 electrolyte with a power density of 0.480 W·cm$^{-2}$ at 700 °C [107]. The substitution of Co with Cu lowered electrical conductivity, but a better thermal compatibility with the electrolyte was achieved. Wang et al. [108] reported a Pr$_2$BaNiMnO$_{7-\delta}$ cathode that showed excellent compatibility with BCZY7111 electrolyte and generated a remarkable MPD of 1.07 W·cm$^{-2}$ at 700 °C with almost negligible degradation after 100 h.

The origin of triple conduction in the double perovskites has been the focus of several studies. EIS as a function of pO$_2$ and pH$_2$O was employed to indicate that, for PrBaCo$_2$O$_{5+\delta}$, protons are involved in the electrochemical process [109]. Compositions with large oxygen-vacancy concentrations for water insertion provide the best cathode performance due to the delocalisation of water from the electrolyte/electrode interface to the electrolyte/gas interface. The substitution of Co with Fe lowers the oxygen-vacancy concentration and, hence, increases the polarisation resistance. Tellez Lozano et al. [110] investigated $^{18}$O and $^2$H diffusion in PBCO at 300 °C by secondary ion mass spectroscopy (SIMS), showing that mixed oxide-ionic–electronic conductivity is retained and that the presence of water gives rise to an enhancement of the surface exchange rate by a factor of 3 compared to pure oxygen. $^2$H diffusion is associated with probable large-scale defects, such as pores, consisting of hydrated Ba compounds. The authors conclude that PBCO and GBCO act principally as MIEC materials in PCFC devices, although proton conductivity may be involved to a small extent. Recent work by Malyshkin et al. [111] also paints a complex picture as regards the location of protons and their role in the electrochemical reaction in double perovskites. The authors indicate that whereas the single-phase, double perovskite

Figure 4. SEM cross-section images of a single cell based on a PBSCF cathode on BZCYYb4411 electrolyte (a); magnification image corresponding to PBSCF interlayer deposited by pulsed laser deposition (PLD); (b) electrochemical performance of the single cell at different temperatures (c); and polarization curves in both electrolysis and fuel cell modes (d). Copyright 2019 by Royal Society of Chemistry [102].
Gd$_{0.8}$La$_{0.2}$Ba$_{0.95}$La$_{0.05}$Co$_2$O$_{6-\delta}$ does not hydrate, the impurity phase BaCo$_{0.8}$Gd$_{0.2}$O$_{3-\delta}$ absorbs a significant amount of water. However, the extent of proton absorption in double perovskites seems to be subtly dependent on composition. SIMS showed that the double perovskite BaGd$_{0.8}$La$_{0.2}$Co$_2$O$_{6-\delta}$ (BGLC) incorporates protons in the bulk, whereas the simple perovskite Ba$_{0.5}$La$_{0.5}$CoO$_3$ (BLC) does not [112]. Nevertheless, a better performance as electrolyser with a SrZr$_{0.5}$Ce$_{0.4}$Y$_{0.1}$O$_{3-\delta}$ electrolyte was observed for BLC. A recent study also adopts the double perovskite Ba$_{1-x}$Gd$_{0.8}$La$_{0.2+x}$Co$_2$O$_{6-\delta}$ as the steam anode in a tubular protonic ceramic electrolysis cell with a low polarisation resistance (<1 $\Omega$·cm$^2$) at 600 °C [113]. Malyshkin et al. [107] suggest that the focus should be shifted to studying the role of exsolved secondary phases on promoting the electrochemical reaction or on the triple-conducting secondary phases themselves, such as BaCo$_{0.8}$Gd$_{0.2}$O$_{3-\delta}$.

Recently, a simple cobaltite perovskite PrNi$_{0.5}$Co$_{0.5}$O$_{3-\delta}$ (PNC) associated with triple-conducting properties was processed with a nanofibre microstructure, leading to a very low polarisation resistance of 0.055 $\Omega$·cm$^2$ at 500 °C and an excellent MPD of 0.611 W·cm$^{-2}$ at 600 °C when operating on BCZYYb4411 electrolyte [114] (Figure 5).

Another simple cobaltite perovskite developed in 2014, around the period that the first double perovskites were reported, is BaCo$_{0.4}$Fe$_{0.4}$Zr$_{0.1}$Y$_{0.1}$O$_{3-\delta}$ (BCFZY). This phase gave an excellent power output of 0.455 W·cm$^{-2}$ at 500 °C due to its triple-conducting character [115]. The same material then demonstrated excellent performance as a cathode in SOFCs with an oxide-ion conducting Ce$_{0.8}$Gd$_{0.2}$O$_{3-\delta}$ electrolyte [116], providing an untypical example of transfer of technology from PCFC to SOFCs. BCFZY was chosen as the cathode in the development of a manufacturing cost model to estimate the production costs of PCFC stack technology using high-volume manufacturing processes [117]. As is the case for double perovskites [105], A-site deficiency in BCFZY increases oxygen deficiency, significantly improving oxygen diffusion and hydration kinetics: an MPD of 0.797 W·cm$^{-2}$ was achieved at 650 °C for the composition Ba$_{0.9}$Co$_{0.4}$Fe$_{0.4}$Zr$_{0.1}$Y$_{0.1}$O$_{3-\delta}$ [118]. B-site deficiency in BCFZY is also reported to enhance performance with a cell containing a Ba(Co$_{0.4}$Fe$_{0.4}$Zr$_{0.1}$Y$_{0.1}$)$_{0.95}$O$_{3-\delta}$ cathode, achieving a power output of 0.840 W·cm$^{-2}$ at 650 °C on a thin-film, B-site-deficient Ba(Zr$_{0.1}$Ce$_{0.7}$Y$_{0.1}$Yb$_{0.1}$)$_{0.95}$O$_{3-\delta}$ electrolyte [119]. On partially replacing Ba by Ca to obtain Ba$_{0.95}$Ca$_{0.05}$Co$_{0.4}$Fe$_{0.4}$Zr$_{0.1}$Y$_{0.1}$O$_{3-\delta}$, Li et al. [120] reduced superficial Ba segregation, improving phase stability and CO$_2$ tolerance, as well as the electrocatalytic performance. Recently, Ni-doped BaCo$_{0.4}$Fe$_{0.4}$Zr$_{0.1}$Y$_{0.1}$O$_{3-\delta}$ was also evaluated with a Ba(Ce$_{0.7}$Zr$_{0.1}$Y$_{0.1}$Yb$_{0.1}$)$_{0.95}$O$_{3-\delta}$ electrolyte, showing improved oxygen mobility, bulk oxide-ion-proton conductivity, and surface exchange kinetics [121].

BCFZY is arrived at through Y-doping of the BaCo$_{0.4}$Fe$_{0.4}$Zr$_{0.2}$O$_{3-\delta}$ cathode discussed in the previous section. Zohourian et al. [122] offer a detailed study of proton uptake in BCFZ using thermogravimetry. The authors conclude that the proton uptake of potential electrode perovskite compositions is much lower than that of proton-conducting electrolyte.

Figure 5. (a) SEM image of a nanofibre-structured PrNi$_{0.5}$Co$_{0.5}$O$_{3-\delta}$ electrode; (b) magnified image of corresponding hollow fibre; (c) single-cell performance of the PNC cathode over a BCZYYb4411 electrolyte and Ni-BCZYYb4411 anode in the range 500–600 °C. Copyright 2020 by Springer Nature [114].
materials, although proton concentrations are sufficient to allow for oxygen reduction to water via bulk protonic transport. The paper goes on to discuss the parameters that come into play on considering the ability of protonation, including the basicity of the oxide ions, charge of the B-site cations and covalency of the B-O bonds. A subsequent study by the same authors extends the TG study to eighteen compositions in the perovskite family (Ba,Sr,La)(Fe,Co,Zn,Y)O$_{3-\delta}$, finding that proton uptake is greatest with Zn on the B-site, while Co has the opposite effect [123]. The Co-free composition Ba$_{0.95}$La$_{0.05}$Fe$_{0.8}$Zn$_{0.2}$O$_{3-\delta}$ hosts the greatest proton concentration, but at the expense of poorer catalytic activity and lower electronic conductivity than the Co-containing compositions. Proton uptake in BCFZY was measured by electrical conductivity relaxation, demonstrating that it occurs via hydrogenation with the sacrifice of holes at high oxygen partial pressure [124].

One of the best performances reported so far for a PCFC single cell is based on Bi and Sn-doped Ba$_{0.5}$Fe$_{0.5}$O$_{3-\delta}$ [125]. The cobalt-free composition BaFe$_{0.5}$Sn$_{0.2}$Bi$_{0.3}$O$_{3-\delta}$ reached an MPD of 1.28 W cm$^{-2}$ on a BCZY71 electrolyte at 700 °C. The introduction of bismuth was shown by X-ray photoelectron spectroscopy to increase the ORR activity, whereas hydration measurements and density functional theory (DFT) calculations indicated that bismuth also enhanced the triple-conducting nature of the ferrite.

5. Composite Cathodes

Composite cathodes consisting of two or more oxide phases with distinct properties have been successfully employed in SOFC research for a considerable number of years [126]. A typical composite consists of the fine-grained electrolyte material with high ionic conductivity mixed with a phase of high electronic conductivity to increase the TPB. The particle size in the porous mixture should be limited to sustain a high purity and the TPB length. It is unsurprising that composite cathodes have been widely adopted in PCFC research, given their ubiquity in oxide-ion-conducting SOFCs. Figure 1d shows a schematic diagram of a composite electrode for a PCFC in its simplest form, consisting of a phase with high electronic conductivity and a phase with high protonic conductivity. The reaction area may be extended considerably through mixed oxide–ionic–electronic conduction or protonic–electronic conduction or triple conduction in one or both components. The performance advantages offered by composite electrodes due to the more precise and ready tailoring of electrochemical and electrocatalytic requirements should be weighed against the greater complexity of the electrode system in terms of component thermal and chemical compatibility between the phases and with other cell components, in addition to greater processing difficulty.

Cobaltite perovskites, such as Sm$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$, have been intensively researched as SOFC cathodes due to their extremely good mixed electron oxide-ion-conducting properties. Therefore, it is unsurprising that such phases have been readily adopted in composite electrodes for protonic ceramic cells. One of the first studies of multiple-component air electrodes for PCFCs constitutes a composite with the more stable proton conductor BaCe$_{0.8}$Sm$_{0.2}$O$_{3-\delta}$ (BCS20) [127]. The interfacial R$_p$ reached a minimum for approximately 60 wt % SSC (0.21 Ω cm$^{-2}$ at 700 °C and MPD of 0.24 W cm$^{-2}$). SSC was then adopted with the more stable proton conductor, rendering an MPD of 0.528 W cm$^{-2}$ at 700 °C with BaCe$_{0.5}$Zr$_{0.3}$Y$_{0.16}$Zn$_{0.04}$O$_{3-\delta}$ also as electrolyte [128]. Daily et al. achieve a very similar MPD, 0.529 W cm$^{-2}$ at 700 °C, employing an SSC-BaCe$_{0.8}$Zr$_{0.1}$Y$_{0.1}$O$_{3-\delta}$ (BCZY81) composite cathode deposited on BZY81 electrolyte by wet powder spraying [129]. BCZY71 electrolyte is replaced by BZY20 to mitigate the reaction between the two ceramic phases in a SSC-BZY20 electrode, which is co-fired in a one-step process with BCZY71 electrolyte, attaining a power density of 0.3 W cm$^{-2}$ at 600 °C [130]. By preparing a fibrous composite cathode of SSC with embedded BaCe$_{0.5}$Zr$_{0.35}$Y$_{0.15}$O$_{3-\delta}$ particles using an electrospinning process, Park et al. achieved a lower polarisation resistance of 0.185 Ω cm$^{-2}$ at 700 °C in comparison to a typical nanocomposite electrode (MPD was 0.64 W cm$^{-2}$ at 700 °C) [131]. Further improvement was achieved by impregnating a Y-doped BaZrO$_3$ (BZY) electrolyte backbone with SSC nanoparticles, reaching an MPD of 0.6 W cm$^{-2}$ at 600 °C [132]. He et al.
employed a composite SSC-BCS20 cathode to study cathode reaction models by impedance spectroscopy as a function of pO2 and pH2O [133]. It was found that the migration of protons to the TPBs and the surface diffusion of adsorbed O species may be rate limiting in wet atmospheres, whereas in dry atmospheres, the rate-limiting steps are likely to be the reduction of Oad to Oad− and surface diffusion of Oad−. A similar SSC-BCS20 electrode composition was used to evaluate the principal parameters for modelling PCFCs by numerical methods, emphasizing the underestimated role of hole conductivity in the electrolyte on simulations, and finding that surface diffusion is rate-limiting [134]. A combined modelling and experimental study of the composite SSC-Ce0.5Sm0.5O2−δ (20SDC) on BCZY71 electrolyte indicated that the surface diffusion of oxide ions is dominant in the reaction order [135]. In 2020, Lv et al. [136] reported a SrCo0.8Fe0.15Zr0.05O3−δ-BCZYYS7111 composite cathode with high structural stability and CO2 tolerance, which exhibited a low Rp value of 0.07 Ω cm−2 at 700 °C and an MPD of 0.71 W cm−2 at 700 °C. A composite cathode composed of a single and a layered perovskite, Sm0.5Sr0.5CoO3−δ-SmBaCo2O5+δ, has recently been reported, showing a low Rp (0.18 Ω cm−2 at 700 °C) and a remarkable MPD of 1.57 W cm−2 at 750 °C [137].

Other perovskite cobalites employed as the MIEC phase in a composite electrode include LaCoO3δ, which was infiltrated into a porous BCZY712 backbone, thereby avoiding detrimental cation interdiffusion, which may occur on high-temperature sintering; a low Rp of 0.11 Ω cm−2 at 600 °C in air was attained [138]. A barium lanthanide cobaltite, Ba4Sr2Sm2Co4O15+, was used in a composite cathode with BaCo0.5Pr0.3Y0.2O3−δ proton conductor, achieving the best performance for a 30:70 wt% Ba4Sr2Sm2Co4O15+/BaCo0.5Pr0.3Y0.2O3−δ ratio, with Ba4Sr2Sm2Co4O15+ serving as an active phase for the dissociative absorption of oxygen; an MPD of 0.197 W cm−2 at 600 °C and stability of Ba4Sr2Sm2Co4O15+ in 1% CO2 in air was reported [139]. The cobaltite composite La0.5Ba0.5CoO3−δ-BaZrO3 was prepared by both a modified Pechini method, followed by exsolution from the previously prepared, single-phase perovskite La0.3Ba0.7Zr0.4Co1.6O3−δ, and by direct calcination of the precursor, with the former process demonstrating an Rp of 1.54 Ω cm−2 at 600 °C [140]. A similar synthesis technique was then employed for the fabrication of La1−xBaxCo3−δ−BaZr0.9Y0.1O2.95 electrodes with direct deposition of the single-phase precursor material on the BaZr0.9Y0.1O3−δ (BZY10) electrolyte [141]; weight ratios of La1−xBaxCo3−δ-BZY10 of 60:40 and 80:20 were associated with Rp values of 0.21 and 0.27 Ω cm−2 at 600 °C, respectively. The cobaltite perovskite SrCo0.2Fe0.2Zr0.1O3−δ (SCF) exhibited high stability in comparison to the Zr-free analogue [142]. A composite of SCFZ and BCZY71 on a BCZY71 electrolyte in fuel-cell reactor mode produced a power output of 0.129 W cm−2 and 91% selective ethylene yield at 21% methane conversion at 700 °C [142].

Composite cathodes with LSCF as the primary electron-hole-conducting component have been employed in numerous studies. One of the earliest examples, by Fabbri et al., reports superior performance of LSCF-BaCe0.9Yb0.1O3−δ (BCY10) cathodes in a ratio of 50:50 wt% with an Rp of 0.14 Ω cm−2 at 700 °C, and better fuel-cell performance in comparison to Pt [143]. Yoo et al. [144] studied the electrochemical performance of symmetrical cells with porous cathodes LSCF, LSCF-BCY10, and LSCF-BZY20 as a function of pO2 and pH2O, observing that the BCY-containing cathode gave the best performance due to extension of the TPB, whereas the poorest performance, exhibited by the LSCF-BZY20 electrode, was attributed to poor proton conductivity along the BZY particles; the ORR was signalled as the principal rate-determining step rather than proton transport. In another study employing electrospinning, BaCe0.5Zr0.35Y0.15O3−δ-embedded LSCF fibrous cathodes were prepared using an LSCF precursor gel containing the BaCe0.5Zr0.35Y0.15O3−δ nanopowder; an anode-supported single cell of this cathode on BaCe0.5Zr0.35Y0.15O3−δ electrolyte provided an MPD of 0.537 Ω cm−2 at 700 °C [145]. The mixed cobaltite–ferrite series Ca4Y1−xFe0.5Co0.5O3−δ exhibits high conductivities (202 S cm−1 at 750 °C for x = 0.3) and excellent compatibility with BCZY71 electrolyte [146] (Figure 6). The power density produced by a Ca0.3Y0.7Fe0.3Co0.3O3−δ-BCZY71 composite cathode on BCZY71 electrolyte was 0.798 W cm−2 at 750 °C [146].
Shimada et al. [147] undertook a performance comparison of cobaltite perovskite electrodes \(La_{0.6}Sr_{0.4}CoO_3-\delta\) (LSC64), \(La_{0.5}Ba_{0.5}CoO_3-\delta\), and LSCF with BCZYYb7111 proton- conducting phase in anode-supported cells with a BCZYYb7111 electrolyte. All three cathodes were chemically compatible with the electrolyte and exhibited stable PCFC performance, with the \(La_{0.6}Ba_{0.4}CoO_3-\delta\)-BCZYYb7111 composite achieving the best power output (1.0 W cm\(^{-2}\) at 700 °C).

As is the case with LSCF, the popular SOFC cathode material BSCF has also been adopted regularly as the mixed oxide-ionic–electron-conducting component of composite PCFC air electrodes. One of the first examples, in 2009, is a BSCF-BCZY71 composite prepared by a modified Pechini method, which provided an MPD of 0.42 W·cm\(^{-2}\) and a low \(R_p\) of 0.1 Ω·cm\(^2\) at 700 °C with a BCZY71 electrolyte [148]. Taillades et al. [149] then showed that a composite BSCF-BCY10 exhibited a lower ASR value (0.53 Ω·cm\(^2\) at 600 °C) compared to pure BSCF. The same group subsequently fabricated a BSCF-BZCYyb7171 cathode deposited on a BCZYYb7111 electrolyte by wet powder spraying, achieving an MPD of 0.422 W·cm\(^{-2}\) at 600 °C [150]. A reversible protonic ceramic cell was developed by Marrony and Dailliy [151] employing a BCZYY81-ZnO (5 mol%) electrolyte and BSCF-BCZYY81 cathode. Although the electrochemical performance was promising in both fuel-cell and electrolyzer modes, the authors note that high temperature, accompanied with high water-vapor partial pressure, can accelerate degradation of the Ba-containing materials. Interestingly, K-doped BSCF, \(Ba_{0.4}K_{0.1}Sr_{0.5}CoO_3-\delta\), exhibited a lower proton migration energy when compared with undoped-BSCF [152]. The composite \(Ba_{0.4}K_{0.1}Sr_{0.5}CoO_3-\delta\)-BCZY71 provided an exceptionally high MPD of 1.275 W·cm\(^2\) at 750 °C, much higher than that obtained for pristine BSCF [152]. Duan et al. [153] performed long-term tests using 11 different fuels, including hydrogen, methane, propane, and ethanol, in NiO-BZY20/BZY20/BCZYYb7111/BCFZY cells between 500 and 600 °C for over 6000 h, observing very low degradation and high resistance to sulphur poisoning. Optimisation of the microstructure of BCFZY cathode, using a low-temperature spray-pyrolysis deposition method, greatly decreased the polarisation resistance to values as low as 0.018 Ω·cm\(^2\) at 700 °C [154].

Although cobalt-containing perovskites, such as LSCF and BSCF, are excellent MIEC components in composite cathodes, there is considerable advantage in replacing Co to mitigate high thermal expansion, carbonation and, to some extent, costs. Thus, ferrite- and manganite-based perovskites have been the focus of attention in composite electrodes as the lower oxide-ion conductivity than that offered by the cobaltite phases may be compensated somewhat by oxide-ion transport in the proton-conducting component of the composite electrode.
Bi et al. [155] employed a component cathode of BaCe$_{0.8}$Sm$_{0.2}$O$_{3-\delta}$ and La$_{0.9}$Sr$_{0.1}$FeO$_{3-\delta}$ (LSF73) on a BaCe$_{0.8}$Sm$_{0.2}$O$_{3-\delta}$ electrolyte, generating an MPD of 0.35 W cm$^{-2}$ at 700 °C, in which the surface was modified by spray-coating to promote adherence of the cathode to the electrolyte. In another study, both composite anode and cathode were prepared by the infiltration of (La$_{0.75}$Sr$_{0.3}$)$_3$Y$_{20.3}$-δ and La$_{0.9}$Sr$_{0.1}$FeO$_{3-\delta}$, respectively, into the proton conductor BaCe$_{0.51}$Zr$_{0.49}$Y$_{0.15}$Zn$_{0.04}$O$_{3-\delta}$ as scaffold, and the cell performance was compared to that of YSZ and Ba(Ce$_{0.51}$Zr$_{0.49}$Y$_{0.15}$Zn$_{0.04}$O$_{3-\delta}$) as electrolyte [156]. Higher power densities were observed for the proton-conducting cell, which were attributable to lower electrode polarisation and lower ohmic resistance of the electrolyte. A comparison of composite electrodes composed of the same H$^+$-conducting phase with La$_{0.8}$Sr$_{0.2}$FeO$_{3-\delta}$ (LSF82) or undoped LaFeO$_3$ (LF) revealed similar performances, implying that the greater oxide-ion conductivity of the LSF82 phase had a minimal effect on the electrode performance [157]. This led the authors to suggest that the role of the hydroxyl ion may be critical in generating oxide ions and water. In a follow-up study [158], a comparison of BaZr$_{0.75}$Y$_{0.15}$O$_{3-\delta}$, BaCe$_{0.75}$Y$_{0.15}$O$_{3-\delta}$, and BaCe$_{0.45}$Zr$_{0.30}$Y$_{0.15}$O$_{3-\delta}$ scaffolds infiltrated with LSF found the best cathode performance for the BaZr$_{0.75}$Y$_{0.15}$O$_{3-\delta}$ and BaCe$_{0.45}$Zr$_{0.30}$Y$_{0.15}$O$_{3-\delta}$ scaffolds. Ren et al. [159] studied the influence of Zr$^{4+}$ doping on the Sr$_2$Fe$_1$Mo$_{0.5}$O$_{6-\delta}$ perovskite, achieving improved proton diffusion kinetics, $D_{\text{H}_2\text{O}}$ = 8.71·10$^{-2}$ cm$^2$ s$^{-1}$, and a low polarisation resistance, 0.169 Ω cm$^{-2}$ (both at 700 °C) for Zr-doped material. Recently, Lei et al. [160] reported a nanostructured Sr$_2$Fe$_{1.5}$Mo$_{0.5}$O$_{6-\delta}$ composite cathode operating in electrolyser mode, with a performance of 0.21 A cm$^{-2}$ at 600 °C and a faradic efficiency of 63.6%.

Another way in which the cathodic reaction differs in PCFCs in comparison to SOFCs is the generation of steam in the cathode. Shin et al. [161] explored the use of small amounts of alkali oxides as steam-generating catalysts, demonstrating that Li$_2$O as catalyst significantly improves the cathodic performance in the range 400–600 °C. The enhancement was attributed to catalytic activity for the dissociative chemisorption and diffusion of reactants on the composite-electrode surface. Sun et al. [162] compared a proton-conducting LSF73-BCZY71 and a proton-blocking LSF73-20SDC cathode over a BCZY71 proton-conducting electrolyte, showing that although LSF73-BCZY71 performed better in polarisation measurements, single cells with the LSF73-20SDC cathode displayed higher OCVs and lower polarisation resistances, achieving an MPD of 0.45 W cm$^{-2}$ at 700 °C. The same group then optimised the LSF73-20SDC cathode in terms of microstructure and electrolyte-interface characteristics, raising the MPD to 0.542 W cm$^{-2}$ at 650 °C [163]. The proton-blocking strategy is further explored with the composite La$_2$NiO$_{4+\delta}$-LaNi$_{0.6}$Fe$_{0.4}$O$_{3-\delta}$ electrode, with a 70:30 wt % mixture showing the lowest ASR and an MPD of 0.590 W cm$^{-2}$ at 700 °C on BCZY71 electrolyte [164]. Another ferrite-based, cobalt-free, composite cathode achieving a high power output is Pr$_{0.95}$Sr$_{0.05}$Cu$_{0.9+\delta}$Fe$_{0.5}$O$_{3-\delta}$-20SDC with MPD values of 0.45 and 0.55 W cm$^{-2}$ at 650 °C on BaCe$_{0.5}$Sr$_{0.5}$O$_{3-\delta}$ and BCZY71 electrolytes, respectively [165]. Further improvement was obtained on using La$_{0.35}$Pr$_{0.15}$Sr$_{0.5}$FeO$_{3-\delta}$ in the composite cathode, reaching a power density of 1.08 W cm$^{-2}$ at 700 °C [166]. Vert et al. [167] studied the ferrite phase Pr$_{0.58}$Sr$_{0.4}$Fe$_{0.8}$Co$_{0.2}$O$_{3-\delta}$ in conjunction with BCY10, reporting the lowest polarisation resistance for a 50:50 vol % mixture. In the series of ferrite-based perovskites Nd$_{0.5}$Ba$_{0.5}$Fe$_{1-x}$Ni$_x$O$_{3-\delta}$ (0 ≤ x ≤ 0.15), the highest conductivity is observed for the x = 0.1 member [168]. A composite cathode of Nd$_{0.5}$Ba$_{0.5}$Fe$_{1-x}$Ni$_x$O$_{3-\delta}$-BCZY71 on BCZY71 electrolyte exhibited a power density of 0.49 W cm$^{-2}$ at 700 °C. The perovskite BaCe$_{0.4}$Fe$_{0.4}$Co$_{0.2}$O$_{3-\delta}$ was prepared as a precursor powder by a modified Pechini method, from which two perovskite phases, referred to as a nanocomposite, were discernible on heat treatment at 900 °C [169]. A single cell of the cathode on BCZYYb17 electrolyte produced an MPD of 0.335 W cm$^{-2}$ at 700 °C. A similar performance of 0.341 W cm$^{-2}$ and a low $R_p$ of 0.1 Ω cm$^2$ at 700 °C was achieved for the cobalt-free composite Sm$_{0.5}$Sr$_{0.5}$FeO$_{3-\delta}$-BCZY71 on BCZY71 electrolyte [170]. One of the best performances of a ferrite-based cobalt-free electrode was reported for the series Ba$_{0.95}$Ca$_{0.05}$Fe$_{0.9+\delta}$Sm$_{0.1}$O$_{3-\delta}$ as a composite phase with SDC, in which Sn-doping was found to enhance electrochemical performance, with the x = 0.05 phase providing an MPD of 0.95 W cm$^{-2}$ at 700 °C on
BCZY71 electrolyte [171]. Liu et al. [172] have recently reported on the ferrite-based series (SrBa)\(_{1-x}\)Pr\(_x\)(CuTi)\(_{0.2}\)Fe\(_{0.8}\)O\(_{3-δ}\), in which the best electrochemical performance is obtained for \(x = 0.4\) in a composite with SDC, achieving an MPD of 0.925 W·cm\(^{-2}\) at 750 °C on BCZY71 electrolyte.

Air electrodes consisting of an oxide-ion-conducting phase and lanthanum manganite-based compositions as the electron-conducting component have been studied throughout the short history of PCFC cathode research. In one of the first such studies, Lin et al. [173] employ a La\(_{0.8}\)Sr\(_{0.2}\)MnO\(_3-δ\)–La\(_{0.5}\)Ce\(_{0.5}\)O\(_{1.75}\) (LSM82-50LDC) composite on an La\(_{0.99}\)Ce\(_{0.01}\)NbO\(_4\) thin electrolyte, and report an MPD of 0.065 W·cm\(^{-2}\) at 800 °C. Kravchyk et al. [54] studied LSM73, LSCM, and BSCF cathodes for a similar LaNbO\(_4\)-based electrolyte, finding that the LSCM cathode was the most chemically and mechanically stable with the lowest electrode polarization resistance. For composite electrodes with LSM82 and LaNbO\(_4\), the lowest electrode polarisation-resistance value (R\(_p = 22\) Ω·cm\(^{-2}\) at 750 °C) was achieved on mixing LSM82 and L\(_{0.995}\)Ca\(_{0.005}\)NbO\(_4\) in a 50:50 vol % ratio. Solis et al. [174] note that in such LSM82-based composites, the protonic phase should exhibit considerable H\(^+\) conductivity, since proton transport through the electrode is rate-limiting. Similarly, LSM82 electrodes in conjunction with La\(_{3}\)WO\(_{12}\)-δ electrolyte were improved substantially upon the addition of the electrolyte material into the LSM82 electrode, thereby increasing the TPB length [175]. The rate-limiting steps in the LSM82-La\(_{3}\)WO\(_{12.25}\)-δ cathode were subsequently attributed to surface-related processes, which could be accelerated by impregnation with nanosized 20SDC particles and by imposing a net current through the electrode [176]. Similarly, the reaction kinetics of LSM82-La\(_{28-x}\)W\(_{4+x}\)O\(_{54+3x/2}\) (\(x = 0.85\) could be accelerated on the addition of Pt nanoparticles [177].

Lee et al. [178] studied the effects of humidification on BaCe\(_{0.85}\)Y\(_{0.15}\)O\(_{3-δ}\) (BCY15)-based cells with LSM82-Ce\(_{0.9}\)Gd\(_{0.1}\)O\(_{2-δ}\) (10GDC) electrodes, observing that reaction sites become occupied by water vapour, thereby increasing the charge-transfer resistance. Replacing the 10GDC component with H\(^+\)-conducting BCY15 increases the effective TPB and mitigates the effects of humidity. Recently, an La\(_{0.5}\)Sr\(_{0.5}\)MnO\(_{3-δ}\) (LSM55)-based cathode in conjunction with K\(_2\)NiF\(_4\)-type layered La\(_{0.5}\)Sr\(_{1.5}\)MnO\(_{4+δ}\) with interstitial oxygen transport was prepared by an in situ co-assembly technique, and exhibited both a much lower R\(_p\) than single-phase LSM55 on BCZY71 electrolyte and an exceptional MPD of 0.94 W·cm\(^{-2}\) at 700 °C [179].

LSM82–BCZY71 composites have also been employed as steam electrodes in electrolysis mode on BCZY71 electrolyte, in which the introduction of nanoparticles with catalytic activity, particularly Pr\(_{0.2}\)O\(_{11}\)-CeO\(_{2}\), lowered the R\(_p\) toward water splitting and oxygen evolution [180]. A similar composition, (La\(_{0.75}\)Sr\(_{0.25}\))\(_{0.5}\)Mn\(_{0.2}\)O\(_{3-δ}\)-BaCe\(_{0.5}\)Zr\(_{0.5}\)Y\(_{0.16}\)Zr\(_{0.04}\)O\(_{3-δ}\), has also been employed for steam electrolysis with a current efficiency of 22% [181].

As discussed in the previous section, layered RP phases and layered perovskites have been associated with triple-conducting properties and excellent air-electrode performances. Unsurprisingly, in the past few years, studies of composites with layered phases have become much more common. One of the first examples employs Nd\(_{1.95}\)NiO\(_{4+δ}\) and BCZY71 electrolyte, in which the introduction of nanoparticles with catalytic activity, particularly Pr\(_{0.2}\)O\(_{11}\)-CeO\(_{2}\), lowered the R\(_p\) observed for 60 wt % of the nickelate at 0.43 Ω·cm\(^{-2}\) at 750 °C and a power density of 0.154 W·cm\(^{-2}\) [182]; the relatively low MPD is attributed to a high electrolyte resistance. Babinec et al. [183] made use of a thick, porous BCZY71 backbone, which was infiltrated with La\(_{2}\)NiO\(_{4+δ}\) nanoparticles for hydrogen-flux measurements. Similarly, nanoparticles of (Pr\(_{0.9}\)La\(_{0.1}\))\(_{2}\)(Ni\(_{0.74}\)Cu\(_{0.21}\)Nb\(_{0.05}\))O\(_{4+δ}\) were infiltrated on the surface of a BCZY71 skeleton with a load of 46 wt % to achieve an MPD of 0.770 W·cm\(^{-2}\) at 700 °C; the cell was operated without degradation for 200 h at 600 °C [184] (Figure 7).

Tarutin et al. [185] employed a Pr\(_{1.4}\)Ba\(_{0.5}\)NiO\(_{4+δ}\)-BaCe\(_{0.5}\)Zr\(_{0.5}\)O\(_{3-δ}\)-composite cathode, which was deposited by tape calendaring and co-sintered in a single step with BaCe\(_{0.5}\)Zr\(_{0.5}\)O\(_{3-δ}\) electrolyte and Ni-BaCe\(_{0.5}\)Zr\(_{0.5}\)O\(_{3-δ}\) anode layers; cell performance was reported as 0.470 W·cm\(^{-2}\) at 600 °C. A similar composite of Pr\(_{2}\)NiO\(_{4}\)-BCZY62 was used in electrolysis mode in a thin film BCZY62-based single cell, achieving a current density of 0.977 A·cm\(^{-2}\) at an electrolyzing potential of 1.3 V [186] (Figure 8).
La$_2$NiO$_{4+\delta}$ has also been used as the scaffold for infiltration with LaNi$_{0.3}$Fe$_{0.4}$O$_3$–δ (LNF) particles, with the cathode achieving an outstanding power output of 0.969 W·cm$^{-2}$ at 700 °C employing an LNF loading of 31 wt % and a BCZY71 electrolyte [187]. Recently, Pikalova et al. [188] obtained an MPD of 0.17 W·cm$^{-2}$ in Pr$_{1-x}$Ca$_x$NiO$_{4+\delta}$ composite cathodes with BaCe$_{0.8}$Gd$_{0.2}$Cu$_{0.01}$O$_{3-\delta}$ as the composite phase and electrolyte; Ca doping is indicated to improve the chemical compatibility and electrochemical performance. Huan et al. [189] employed a composite of the layered RP phase SrEu$_2$Fe$_{1.8}$Co$_{0.2}$O$_{7-\delta}$ and BCZY71 as an air electrode for reversible proton-conducting solid oxide cells, which showed no degradation over 135 h under both oxidising and reducing conditions; an MPD of 0.562 W·cm$^{-2}$ at 700 °C was reported in fuel-cell mode.

Other triple-conducting oxides, which have been adopted in a composite architecture, include double perovskites of the type A'`A''B`B''O$_{5+\delta}$. In a study aimed at improving the durability of PCFCs, Park et al. [190] employed a composite cathode of NdBa$_{0.5}$Sr$_{0.5}$Co$_{0.1}$Fe$_{0.5}$O$_{5+\delta}$–Ce$_{0.5}$Nd$_{0.5}$O$_{2-\delta}$ with a BCZY7111 electrolyte, noting that the deleterious effects of water vapour on cathode degradation can be essentially avoided by a series of operational protocols, which simulate a cathode potential to zero during operation, thereby minimising the effect of high pO$_2$ and pH$_2$O producing undesirable oxide phases on the cathode surface (Figure 9).

Nd$_5$(Ba$_{0.75}$Ca$_{0.25}$)Co$_{1.5}$Fe$_{0.4}$Ni$_{0.1}$O$_{5+\delta}$ was prepared as a composite with both BCZY7111 and Ce$_{0.6}$Gd$_{0.4}$O$_{2-\delta}$ in the weight ratio 6:4, with the latter composite providing the better performance with a peak power density of 0.88 W·cm$^{-2}$ on an anode-supported cell with
BCZYYb7111 electrolyte [191]. Additionally, NdBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+δ} was studied as an electrode in an electrolyser based on BCZYYb7111, reaching 3.16 A·cm^{-2} at 1.3 V and 750 °C in H₂ [192].

The composite PrBaCo_{2}O_{5+δ}–BCZYYb7111 was prepared by impregnating a BCZYYb7111 scaffold with PrBaCo_{2}O_{5+δ} over five cycles. The optimal PBCO loading was ascertained at 36 wt % PBCO, leading to an MPD of 0.49 W·cm^{-2} at 750 °C [193]. Ta-doped PrBaCo_{2}O_{5+δ} cathodes showed improved chemical stability and higher resistance to CO₂ [194]. In addition, composite cathodes of PrBa_{0.9}Ca_{0.1}Co_{2−x}Zn_{x}O_{5+δ} and BCZYYB7111, as reported by Liu et al. [195], showed a higher concentration of oxygen vacancies after Zn-doping of the double perovskite, which resulted in a higher power output of 0.87 W·cm^{-2} for the x = 0.15 composition at 750 °C in comparison to 0.33 W·cm^{-2} for the Zn-free composite.

Figure 8. SEM image of a protonic ceramic electrolysis cell based on a Pr₂NiO₄–BCZY62 composite as anode, BCZY62 as electrolyte, and Ni–BCZY62 as cathode (a); magnified anode component and corresponding anode–electrolyte interface (b); impedance spectra of the half cell in three-electrode configuration with Pr₂NiO₄–BCZY62 composite anode in air at 550 °C with different humidifications (c); current–voltage curves of the single cell in electrolysis mode, with dry H₂ fed to the cathode and 40% of wet air to the anode, in the range 550–700 °C (d). Copyright 2018 by Royal Society of Chemistry [186].

The triple-conducting, simple perovskite BaCo₀.₄Fe₀.₄Zr₀.₃Y₀.₁O₃−δ, prepared with 10 at % Ba deficiency to improve chemical stability in CO₂- and H₂O-containing atmospheres, was employed in a composite with BCZY71 on a BCZY71 electrolyte [196]. Polarisation losses decreased on addition of the BCZY71 proton conductor as a component of the composite electrode, which was attributed to improved oxygen gas adsorption and dissociation, in addition to an enhanced diffusion of oxygen species; an MPD of 0.537 W·cm⁻² was
achieved with the composite at 700 °C. A cobalt-free, triple-conducting simple perovskite $\text{Ba}_{0.95}\text{La}_{0.05}\text{Fe}_{1.8}\text{Zn}_{0.2}\text{O}_{3-\delta}$, used in a composite with BCZYYb7111, reached a single-cell power density of 0.329 W·cm$^{-2}$ at 750 °C [197]. Distribution of Relaxation Times (DRT) analyses of EIS results were employed to indicate that below 650 °C, the rate-limiting steps in the cathodic reaction are the incorporation of oxygen in the lattice and proton bulk diffusion to the TPBs.

A limited number of studies have extended the composite concept to three-component phases. Chen et al. [198] generalised percolation theory for PCFC composite cathodes with different types of mixed-conducting characteristics for binary composites and for the case of an LSCF–SDC–BZCY ternary composite cathode, highlighting the importance of microstructure on the overall performance. Li et al. [199] designed a three-component cathode composed of a $\text{PrBaCo}_2\text{O}_{5+\delta}$–BCZY71 backbone, which was infiltrated with 10GDC particles to enhance oxide-ion transport. A single-cell test with 29.6 wt % 10GDC infiltrated PBCO–BCZY71 provided an extremely high-power density of 1.02 W·cm$^{-2}$ at 700 °C and a very low $R_p$ of 0.051 Ω·cm$^2$, demonstrating the promise of such an approach. However, strong interdiffusion of Pr and Sm was found for a composite of PBCO and 20SDC, and stability of PBCO with CO$_2$ from the air may be an issue [200]. Selected electrode and single-cell performances are provided in Table 3.

**Figure 9.** Schematic diagram of electrochemical potential levels during single-cell operation and operational protocol to prevent cathode surface degradation (a); scanning electron micrograph of a protonic ceramic single cell based on a $\text{NdBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.8}\text{Fe}_{0.5}\text{O}_{3-\delta}$–$\text{Nd}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ composite cathode over a BCZYYb7111 electrolyte and NiO-BCZYYb7111 anode (b); performance of the PCFC before and after operation for different periods of time under a galvanostatic condition of 0.5 A·cm$^{-2}$ at 650 °C for (c) an unprotected cell and (d) for a cell protected using operation protocols with cathode air depletion and shunt current. Copyright 2019 by American Chemical Society [190].
### Table 3. PCFC performances reported in the literature with various electrolytes and cathode components.

| Air Electrode | ASR (Ω·cm²) | MPD (W·cm⁻²) | Electrolyte | Thickness (µm) | Ref  |
|---------------|-------------|--------------|-------------|----------------|-----|
| **Mixed proton–electron-conducting cathodes** | | | | | |
| BaCe₀.₉Zr₀.₁Y₀.₁O₃⁻δ | 0.21 (700 °C) | 0.24 (700 °C) | BCZYB7111 | 30 | [33] |
| BaCe₀.₉Pr₀.₁Gd₀.₁O₃⁻δ | 0.47 (800 °C) | - | BCG20 | 510 | [21] |
| BaFe₀.₈In₀.₂O₃⁻δ | 0.09 (700 °C) | 0.55 (700 °C) | BCZYB7111 | 15 | [25] |
| BaZr₀.₂Fe₀.₈Y₀.₂O₃⁻δ | 0.28 (700 °C) | 0.32 (700 °C) | BCZY71 | 20 | [32] |
| BaZr₀.₆Co₀.₄O₃⁻δ | 0.19 (700 °C) | - | BCZY53 | 20 | [31] |
| **Mixed oxide-ion–electron-conducting cathodes** | | | | | |
| Ba₅₋ₓLa₅₋ₓCo₅₋ₓO₃ | 1.4 (600 °C) | - | Ba(Zr₀.₆Ce₀.₄)₉₋₅O₃⁻δ | 12 | [45] |
| Ba₀.₄Sr₀.₆Fe₀.₄Zr₀.₆O₃⁻δ | 0.08 (700 °C) | 0.48 (700 °C) | BCZY71 | 15 | [62] |
| BaCo₀.₅Fe₀.₅Ce₀.₅Gd₀.₅O₃⁻δ | 0.12 (650 °C) | 0.66 (700 °C) | BCZYB7111 | 30 | [57] |
| BaCo₁₋ₓFeₓ₀.₅Co₀.₅O₃⁻δ | 0.13 (650 °C) | 0.64 (700 °C) | BCZYB7111 | 30 | [57] |
| BaCo₀.₅Fe₀.₅Zr₀.₅O₃⁻δ | 1.0 (600 °C) | 0.22 (600 °C) | BCZYB7111 | 60 | [56] |
| BSCF | 0.06 (700 °C) | 0.80 (700 °C) | Ba(Zr₀.₄Ce₀.₄)₉₋₅O₃⁻δ | 15.5 | [53] |
| Ca₅Co₅O₉ | 0.17 (700 °C) | 0.29 (700 °C) | BCZY53 | 20 | [69] |
| Ca₀.₃₋ₓLa₀.₇Co₄O₉ | (x = 0, 0.3) | 2.2 (600 °C) | - | BCY10 | - | [68] |
| La₀.₄Ba₀.₆Co₁₋ₓO₃⁻δ | - | 0.18 (1000 °C) | BCS10 | 500 | [39] |
| LSC55 | 0.38 (700 °C) | 0.30 (700 °C) | BCZY71 | 500 | [40] |
| LSCF | - | 0.070 (700 °C) | BCZY27 | 20 | [47] |
| LSCF | - | 0.018 (600 °C) | BCZY62 | 500 | [48] |
| LSCF | 1.12 (700 °C) | 0.26 (700 °C) | BCZYB7111 | 60 | [49] |
| LSCF: BaCo₁₋ₓFeₓO₃ | 0.29 (700 °C) | 0.40 (700 °C) | BCZYB7111 | 60 | [49] |
| LSCF | 0.26 (700 °C) | 0.75 (700 °C) | BaCo₀.₉Tb₀.₁O₃⁻δ | 12–15 | [46] |
| Nd₀.₈Ba₀.₂Fe₀.₄Co₀.₁O₃⁻δ | 0.18 (700 °C) | 0.39 (700 °C) | BCZY53 | 30 | [63] |
| SrCo₀.₃Nb₀.₇O₃⁻δ | 0.09 (700 °C) | 0.34 (700 °C) | BCZY44 | 20 | [44] |
| SrCo₀.₃Sb₀.₇O₃⁻δ | 0.14 (700 °C) | 0.25 (700 °C) | BCZY71 | 20 | [42] |
| SrFe₀.₉Nb₀.₁O₃⁻δ | 0.23 (650 °C) | 0.53 (650 °C) | BCZY71 | 20 | [61] |
| SSC | 10 (700 °C) | 5.9·10⁻³ (700 °C) | BCZY62 | 500 | [43] |
| Y₀.₈Ca₀.₂BaCo₄O₇ | 0.12 (700 °C) | 0.47 (700 °C) | BCZY71 | 20 | [65] |
| Y₀.₉Ca₀.₁BaCo₄O₇ | - | 0.30 (725 °C) | BCZY53 | 30 | [66] |
| **Triple protonic oxide electron hole-conducting oxides** | | | | | |
| Ba(Co₁₋ₓFeₓ)₂Zr₀.₁Y₀.₁O₁₋ₓO₃⁻δ | 0.80 (550 °C) | 0.84 (650 °C) | Ba(Zr₀.₄Ce₀.₄)₉₋₅O₃⁻δ | 12 | [119] |
| Ba(Zr₀.₁Co₁₋ₓY₀.₉Yb₀.₁)₀.₉₃O₃⁻δ | 0.61 (550 °C) | 0.45 (550 °C) | BCZYB7111 | 25 | [121] |
| Ba₁₋ₓCa₀.₉Co₀.₃Fe₀.₇Zr₀.₁Y₀.₁O₃⁻δ | 0.36 (700 °C) | 0.58 (700 °C) | BCZYB4411 | 22 | [120] |
| Ba₅₋ₓCo₀.₅FeₓZr₀.₅O₅ | 0.52 (600 °C) | 0.79 (650 °C) | BCZY71 | 40 | [118] |
| BaCo₁₋ₓFeₓZr₀.₁Y₀.₁O₃⁻δ | - | 0.45 (500 °C) | BCZYB7111 | 20–30 | [115] |
| BaFe₀.₉Sn₀.₃Zr₀.₁O₃⁻δ | 0.03 (700 °C) | 1.28 (700 °C) | BCZY71 | 12 | [125] |
| BaFe₀.₉Sn₀.₃Zr₀.₃O₃⁻δ | 0.05 (650 °C) | - | BCZY71 | - | [100] |
| BSCF | 0.18 (650 °C) | 0.62 (650 °C) | BCZYB7111 | 21.3 | [106] |
| GBCO | 0.16 (700 °C) | 0.26 (700 °C) | BCZY71 | 10 | [94] |
| GdBaCuCoO₂⁺⁺ | 0.17 (700 °C) | 0.48 (700 °C) | BCZY71 | 20 | [107] |
| La₁₋ₓSr₀.₈Ni₀.₈Fe₀.₄O₅₋δ | 0.08 (700 °C) | 0.78 (700 °C) | BCZY71 | 15 | [86] |
### Table 3. Cont.

| Air Electrode | ASR (Ω·cm²) | MPD (W·cm⁻²) | Electrolyte | Thickness (μm) | Ref |
|---------------|-------------|--------------|-------------|----------------|-----|
| La₁.₃Ca₀.₇NiO₄₋₃ | 0.05 (700 °C) | 0.923 (700 °C) | BCZY71 | 15 | [87] |
| La₂Ni₄₋₃Fe₁₀O₁₉ | 0.15 (700 °C) | 0.398 (700 °C) | BCZY53 | 20 | [88] |
| LaBaCuCoO₅₀ₓ | 0.15 (700 °C) | 0.432 (700 °C) | BCZY71 | 20 | [97] |
| LaBaCuFeO₅₁ₓ | 0.27 (700 °C) | 0.327 (700 °C) | BCZY71 | 20 | [97] |
| LaNi₀.₆Fe₀.₄O₃₋₅ | 0.13 (700 °C) | 0.550 (700 °C) | BCZY71 | 15 | [90] |
| LiNi₀.₆Co₀.₂O₂ | 3.48 (650 °C) | 0.410 (650 °C) | BCZY71 | 24 | [92] |
| NBSCF | 0.08 (700 °C) | 1.370 (700 °C) | BCZY71 | 14.7 | [98] |
| Nd₂Ni₄₋₅ | 4.8 (600 °C) | 0.060 (600 °C) | BCY10 | 25 | [79] |
| PBSCF | 0.13 (600 °C) | 0.500 (500 °C) | BCZY71 | 15 | [101] |
| PBSCF | 0.30 (600 °C) | 0.650 (600 °C) | BCZY71 | 7.6 | [103] |
| PBSCF | - | 1.100 (600 °C) | BCZY71 | 15 | [102] |
| Pr₂BaNiMnO₇₋₈ | 0.084 (700 °C) | 1.070 (700 °C) | BCZY71 | 20 | [108] |
| Pr₂NiO₅₋₇ | 0.70 (650 °C) | 0.130 (650 °C) | BCY10 | 85 | [77] |
| Pr₂NiO₅₋₇ | 0.06 (650 °C) | 0.820 (650 °C) | BaCe₀.₅Zr₀.₅Y₀.₁5O₃₋₄ | 5 | [82] |
| (PrBa₀.₃Ca₀.₇)₀.₉CuO₆₋₅ | 0.14 (600 °C) | 0.540 (600 °C) | BCZY71 | 20 | [105] |
| PrNi₀.₂₅Co₀.₅O₅₋₇ | 0.05 (500 °C) | 0.611 (600 °C) | BCZY71 | 10 | [114] |
| SmBa₀.₅Y₀.₅CoO₅₋₄ | 0.08 (700 °C) | 0.533 (700 °C) | BCZY71 | 15 | [97] |
| SmBaCoO₄₋₁ₓ | 0.15 (700 °C) | 0.382 (700 °C) | BCZY71 | 25 | [95] |
| Sr₂Fe₀.₃Mg₀.₄Zr₀.₄O₆₋₅ | 0.17 (700 °C) | 0.790 (700 °C) | BCZY71 | 20 | [159] |
| Sr₂Se₀.₃Nb₂₀.₃Co₀.₃Fe₀.₃O₆₋₅ | 0.14 (650 °C) | 0.840 (650 °C) | BCZY71 | 18.5 | [106] |

**Composite cathodes**

| Air Electrode | ASR (Ω·cm²) | MPD (W·cm⁻²) | Electrolyte | Thickness (μm) | Ref |
|---------------|-------------|--------------|-------------|----------------|-----|
| Ba₀.₄K₀.₆Sr₀.₃Co₀.₇Fe₀.₂O₅₋₅ | 0.05 (700 °C) | 1.275 (750 °C) | BCZY71 | 10 | [152] |
| Ba₀.₆Co₀.₄O₂₋₁ₓS₀.₂₀₅₀₁₀Y₀.₁₅O₃₋₄ | 0.05 (700 °C) | 0.950 (700 °C) | BCZY71 | 17 | [171] |
| Ba₀.₆Pr₀.₄Zr₀.₄O₃₋₅ | 0.08 (750 °C) | 0.330 (750 °C) | BCZY71 | 42 | [197] |
| Ba₀.₆Co₀.₄Fe₀.₂Zr₀.₄Y₀.₁₀₁₀O₃₋₄ | 0.15 (700 °C) | 0.540 (700 °C) | BCZY71 | 25 | [196] |
| Ba₀.₂Sr₀.₈Sm₀.₂CoO₅₋₅ | 0.20 (600 °C) | 0.197 (600 °C) | BCY10 | 60 | [139] |
| BaCe₀.₅Fe₀.₄Co₀.₁O₅₋₄ | 0.075 (700 °C) | 0.335 (700 °C) | BCZY71 | 70 | [169] |
| BaCo₀.₄Fe₀.₂Zr₀.₂Y₀.₁₇₁₀O₃₋₅ | 0.25 (600 °C) | 0.660 (600 °C) | BCZY71 | 10–20 | [153] |
| BSCF: BCY10 | 0.53 (600 °C) | 0.293 (700 °C) | BCY10 | 15 | [149] |
| BSCF: BCZY71 | 0.10 (700 °C) | 0.420 (700 °C) | BCZY71 | 20 | [148] |
| BSCF: BCZY71 | 0.27 (600 °C) | 0.420 (600 °C) | BCZY71 | 4 | [150] |
| Ca₀.₃Y₀.₇Fe₀.₃Co₀.₃O₅₋₅ | 0.07 (750 °C) | 0.798 (750 °C) | BCZY71 | 150 | [146] |
| La₀.₈Pr₀.₂₅Sr₀.₅FeO₃₋₅ | 0.06 (700 °C) | 1.080 (700 °C) | BCZY71 | 18 | [166] |
| La₀.₈Ba₀.₂CoO₃₋₅ | 1.₅₄ (600 °C) | 0.060 (600 °C) | BZY10 | - | [140] |
| La₀.₈Ba₀.₂CoO₃₋₅ | 1.₇₆ (600 °C) | 0.060 (600 °C) | BZY10 | - | [140] |
| La₀.₅Sr₀.₅MnO₄₋₅ | 0.08 (700 °C) | 0.940 (700 °C) | BCZY71 | 12 | [179] |
| La₀.₈Sr₀.₂₃CoO₅₋₄ | 0.21 (600 °C) | 0.060 (600 °C) | BZY10 | - | [141] |
| La₀.₈Ba₀.₂CoO₃₋₅ | 0.02 (700 °C) | 1.₀₀₀ (700 °C) | BCZY71 | 10 | [147] |
| La₀.₈NiO₄₋₅ | 0.09 (700 °C) | 0.590 (700 °C) | BCZY71 | 20 | [164] |
| La₀.₈NiO₄₋₅ | 6.₇ (700 °C) | 0.032 (700 °C) | BCZY71 | 25 | [183] |
| La₀.₈NiO₄₋₅ | 0.03 (700 °C) | 0.969 (700 °C) | BCZY71 | - | [187] |
### Table 3. Cont.

| Air Electrode | ASR (Ω·cm²) | MPD (W·cm⁻²) | Electrolyte | Thickness (µm) | Ref |
|---------------|-------------|--------------|--------------|----------------|-----|
| LaCoO₃: BCZY71 | 0.11 (600 °C) | - | BCZY71 | - | [138] |
| LSCF: BaCe₀.₇Zr₀.₃Y₀.₁₅O₃₋₈ | 0.18 (700 °C) | 0.537 (700 °C) | BaCe₀.₇Zr₀.₃Y₀.₁₅O₃₋₈ | 8 | [145] |
| LSCF: BCYb10 | 0.14 (700 °C) | 0.050 (700 °C) | BCYb10 | 15–20 | [143] |
| LSCF: BCY10 | 0.49 (600 °C) | - | BZY20 | - | [144] |
| LSF73: 20SDC | 0.074 (650 °C) | 0.542 (650 °C) | BCZY71 | 13 | [163] |
| LSF73: BCZY71 | 0.13 (700 °C) | 0.450 (700 °C) | BCZY71 | 15 | [162] |
| LSF82: Ba(Ce₀.₇Y₀.₃Zr₀.₃Zr₀.₁₅O₃₋₈ | 0.09 (700 °C) | 0.425 (700 °C) | Ba(Ce₀.₇Y₀.₃Zr₀.₃Zr₀.₁₅O₃₋₈ | 70 | [156] |
| LSM82: La₀.₉₉5Ca₀.₀₂₅NbO₄ | 25 (750 °C) | - | La₀.₉₉5Ca₀.₀₂₅NbO₄ | - | [174] |
| LSM82: La₈₋ₓCaₓWO₁₂₋₄ | 8 (750 °C) | - | La₈₋ₓCaₓWO₁₂₋₄ | - | [175] |
| LSM82: BCY15 | 0.11 (750 °C) | 0.394 (750 °C) | BCY15 | 15 | [178] |
| LSM82: Laₓ₃WO₁₁₋₂₅ | 1.4 (750 °C) | - | Laₓ₃WO₁₁₋₂₅ | - | [177] |
| LSM2: Laₓ₂₋₄₋ₓW₄₋ₓO₁₄₋₃ₓ | 40 (650 °C) | - | Laₓ₂₋₄₋ₓW₄₋ₓO₁₄₋₃ₓ | - | [177] |
| LSM2: SDC | 0.69 (800 °C) | 0.065 (800 °C) | La₀.₉₉Ca₀.₀₁NbO₄ | 20 | [173] |
| LSM2: BCZY71: Pr | 0.33 (700 °C) | - | BCZY71 | - | [180] |
| Nd₆₋₅₋ₓ₋₄₋ₓ/xCo₁₋₅₋ₓ₋₄₋ₓ¹₋₄₋ₓₓFe₄₋ₓ₋₄₋ₓₓNiₓ₋₄₋ₓ₋₄₋ₓₓO₁ₓ₋₄₋ₓ₋₄₋ₓₓ | 0.091 (650 °C) | 0.880 (650 °C) | BCZY6111 | 20 | [191] |
| Nd₀.₅₋₅₋ₓ₋₄₋ₓ/xCo₁₋₅₋ₓ₋₄₋ₓₓFe₄₋ₓ₋₄₋ₓₓNiₓ₋₄₋ₓ₋₄₋ₓₓ | 0.15 (700 °C) | 0.490 (700 °C) | BCZY71 | 40 | [151] |
| Nd₀.₅₋₅₋ₓ₋₄₋ₓ/xCo₁₋₅₋ₓ₋₄₋ₓₓFe₄₋ₓ₋₄₋ₓₓNiₓ₋₄₋ₓ₋₄₋ₓₓ | 0.15 (700 °C) | 0.490 (700 °C) | BCZY71 | 40 | [168] |
| Nd₀.₅₋₅₋ₓ₋₄₋ₓ/xCo₁₋₅₋₄₋ₓₓNiₓ₋₄₋ₓ₋₄₋ₓₓ | 0.43 (750 °C) | 0.154 (750 °C) | BCZY71 | 60 | [182] |
| Nd₀.₅₋₅₋ₓ₋₄₋ₓ/xCo₁₋₅₋₄₋ₓₓNiₓ₋₄₋ₓ₋₄₋ₓₓ | 0.18 (650 °C) | 0.719 (650 °C) | BCZY71 | 20 | [190] |
| Pr₁₋ₓLaₓO₁₋ₓ₋₄₋ₓ₋₄₋ₓ₋₄₋ₓₓ (Nd₀.₃₋₅₋ₓ₋₄₋ₓₓO₀.₁ₓ₋₄₋ₓₓCa₀.₁ₓ₋₄₋ₓₓO₀.₁ₓ₋₄₋ₓₓ) | 0.13 (700 °C) | 0.770 (700 °C) | BCZY71 | 12 | [184] |
| Pr₁₋ₓLaₓO₁₋ₓ₋₄₋ₓ₋₄₋ₓ₋₄₋ₓₓ (Nd₀.₃₋₅₋ₓ₋₄₋ₓₓO₀.₁ₓ₋₄₋ₓₓCa₀.₁ₓ₋₄₋ₓₓO₀.₁ₓ₋₄₋ₓₓ) | 0.26 (700 °C) | 0.170 (700 °C) | BaCe₀.₅₋ₓ₋₄₋ₓₓGdₓ₋₄₋ₓₓCu₀.₀₁₋₄₋ₓₓO₁₋₄₋ₓₓ | 25 | [188] |
| Pr₁₋ₓLaₓO₁₋ₓ₋₄₋ₓ₋₄₋ₓ₋₄₋ₓₓ (Nd₀.₃₋₅₋ₓ₋₄₋ₓₓO₀.₁ₓ₋₄₋ₓₓCa₀.₁ₓ₋₄₋ₓₓO₀.₁ₓ₋₄₋ₓₓ) | 0.43 (700 °C) | 0.470 (700 °C) | BaCe₀.₅₋ₓ₋₄₋ₓₓZrₓ₋₄₋ₓₓDy₀.₀₁₋₄₋ₓₓO₁₋₄₋ₓₓ | 30 | [185] |
| Pr₂₋ₓNiO₄₋ₓ₋₄₋ₓₓ | 0.31 (700 °C) | 0.977 (700 °C) | BCZY62 | 20 | [186] |
| Pr₀.₅₋ₓCaₓCo₁₋₅₋ₓ₋₄₋ₓₓZrₓ₋₄₋ₓₓO₁ₓ₋₄₋ₓₓ | 0.04 (750 °C) | 0.870 (750 °C) | BCZY71 | 17 | [195] |
| PrBaCo₀.₇₅Ta₀.₂₅O₃₋₄₋₄₋ₓₓ | 0.05 (700 °C) | 0.755 (700 °C) | BCZY71 | 10 | [194] |
| Sr₂₋ₓFe₁₋ₓ₋₄₋ₓₓM₀.₀₁₋₄₋ₓₓO₄₋ₓₓ | 0.48 (600 °C) | - | BZY20 | 16 | [160] |
| (SrBaₓ₋₀₋₄₋ₓₓPr₁₋ₓ₋₄₋ₓₓ₄₋ₓₓFeₓ₋₄₋ₓₓOₓ₋₄₋ₓₓ | 0.07 (750 °C) | 0.925 (750 °C) | BCZY71 | 13 | [172] |
| Sr₄₋ₓ₋₄₋ₓₓCoₓ₋₄₋ₓₓZrₓ₋₄₋ₓₓO₁₋₄₋ₓₓ | 0.13 (700 °C) | 0.560 (700 °C) | BCZY71 | 15 | [189] |
| SSC: BaCe₀.₇Zr₀.₃Y₀.₁₅O₃₋₈ | 0.18 (700 °C) | 0.642 (700 °C) | BaCe₀.₇Zr₀.₃Y₀.₁₅O₃₋₈ | 10 | [131] |
| SSC: BaCe₀.₅₋ₓ₋₄₋ₓₓZrₓ₋₄₋ₓₓY₀.₁₅₋ₓ₋₄₋ₓₓO₃₋₄₋ₓₓ | 0.15 (700 °C) | 0.528 (700 °C) | BaCe₀.₅₋ₓ₋₄₋ₓₓZrₓ₋₄₋ₓₓY₀.₁₅₋ₓ₋₄₋ₓₓO₃₋₄₋ₓₓ | 20 | [128] |
### Table 3. Cont.

| Air Electrode | ASR (Ω·cm\(^2\)) | MPD (W·cm\(^{-2}\)) | Electrolyte | Thickness (µm) | Ref |
|---------------|-------------------|----------------------|-------------|----------------|-----|
| SSC: BCS20    | 0.21 (700 °C)     | 0.240 (700 °C)       | BCS20       | 70             | [127]|
| SSC: BZY20    | 0.3 (600 °C)      | 0.300 (600 °C)       | BCZY71      | 20             | [130]|
| SSC: BCZY81   | 0.10 (700 °C)     | 0.529 (700 °C)       | BCZY81      | 9              | [129]|
| SSC: BZY20    | 0.30 (600 °C)     | 0.300 (600 °C)       | BCZY71      | 20             | [130]|
| SSC: BZY20    | 0.08 (600 °C)     | 0.600 (600 °C)       | BZY20       | 15             | [132]|
| SSC: SmBaCo\(_{2}\)O\(_{5+\delta}\) | 0.02 (750 °C) | 1.570 (750 °C)       | BCZYb7111   | 30             | [137]|
| SSF: BCZY71   | 0.10 (700 °C)     | 0.341 (700 °C)       | BCZY71      | 20             | [170]|

### 6. Summarising Remarks

The cathode is generally recognized as critical for the performance of solid oxide fuel cells, and even more so for the proton-conducting class of ceramic devices. The lower working temperature of protonic ceramic fuel cells places greater demands on the cathode with regard to high catalytic activity and electronic conductivity, even though the lower temperature favours thermal and chemical compatibility between cell components. The earliest studies of PCFC cathodes, dating back to the mid-1990s, parallel SOFC research, with the employment of simple perovskites based on ferrites and cobaltites, and, to a much lesser extent, manganites. Nevertheless, the cathode reactions differ between oxide-ion- and proton-conducting systems. The reaction steps for the overall reduction reaction occurring in a proton-conducting cathode compartment seem to be fairly intuitive, but a clear picture of the rate-determining steps has not emerged. There is widespread agreement that high electron-hole conductivity is essential for a good electrode performance, and good surface proton conductivity is also often recognized as important. Nevertheless, excellent performances have been achieved with “proton-blocking” electrodes, for which it is proposed that the lower level of hydration in the cathode leads to a lower water vapour partial pressure and higher cell potential. A similar argument suggests that high proton conductivity is not necessarily important provided oxide-ion conductivity is high.

The different nature of the cathode reactions between the oxide-ion and proton-conducting systems has driven the pursuit of alternative approaches for PCFC cathode compositions beyond the classical SOFC perovskites. One of the most prominent strategies, focusing on the proton-conducting character of the cathode, has been to dope established proton conductors, typically Ba(Ce,Y)O\(_{3-\delta}\), Ba(Zr,Y)O\(_{3-\delta}\), with multivalent cations, such as Co and Pr, to enhance the electronic-transport component. However, this approach has met with only limited success, since the electronic conductivity and phase stability are generally not sufficient for electrode applications.

The analogy to cathode SOFC research extends to a wide adoption of composite electrodes with different oxide phases providing the electronic and ionic requirements. Very good performances have been achieved with a wide variety of composites, despite their greater complexity in terms of transport properties, microstructure, and compatibility. High power densities have also been achieved for monophase air electrodes, particularly more recently for so-called triple-conducting compositions, with contributions to transport from electron holes, oxide ions, and protons. Mostly, such phases are recognized mixed ionic-electronic conductors with layered perovskite and Ruddlesden–Popper-type structures, such as Pr\(_2\)NiO\(_{4+\delta}\) and PrBaCo\(_{2}\)O\(_{5+\delta}\), which have generally been first adopted in SOFC research. The true nature of transport with the three co-existing species has been a source of debate, since some studies indicate that the protonic contribution may arise from secondary phases or surface reactions. However, it is difficult to reach generalisations covering an entire class of materials as, in some cases, the evidence for bulk triple conduction is convincing.
The evolution of maximum power densities for protonic ceramic single cells since 2008 is shown in Figure 10, where a trend toward generally higher outputs and their more frequent reports can be discerned in the last few years.

![Figure 10. Evolution of reported maximum power densities at 700 °C for protonic ceramic fuel cells.](image)

Future research endeavours are likely to increasingly focus on triple-conducting phases due to their outstanding performances. The employment of infiltrated elements with high catalytic activity has proven to be successful in a limited number of studies, and is also likely to be a popular future route to achieving better cathode performance. The cost and long-term stability of cathode compositions should be an area of concern in future works if the promise of protonic ceramic fuel cells is to be realised.

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