

Perspectives on Cathodes for Protonic Ceramic Fuel Cells

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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, unnecessary 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



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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.

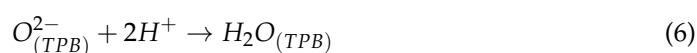
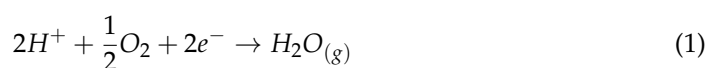
Consequently, there has been much research effort dedicated to lowering the operation temperature of SOFCs to better address small-scale applications (micro SOFCs and auxiliary power units) and reduce the costs associated with fabrication and operation [4]. In particular, a running temperature of 600 °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].

Table 1. General abbreviations.

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		

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 °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:



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

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).

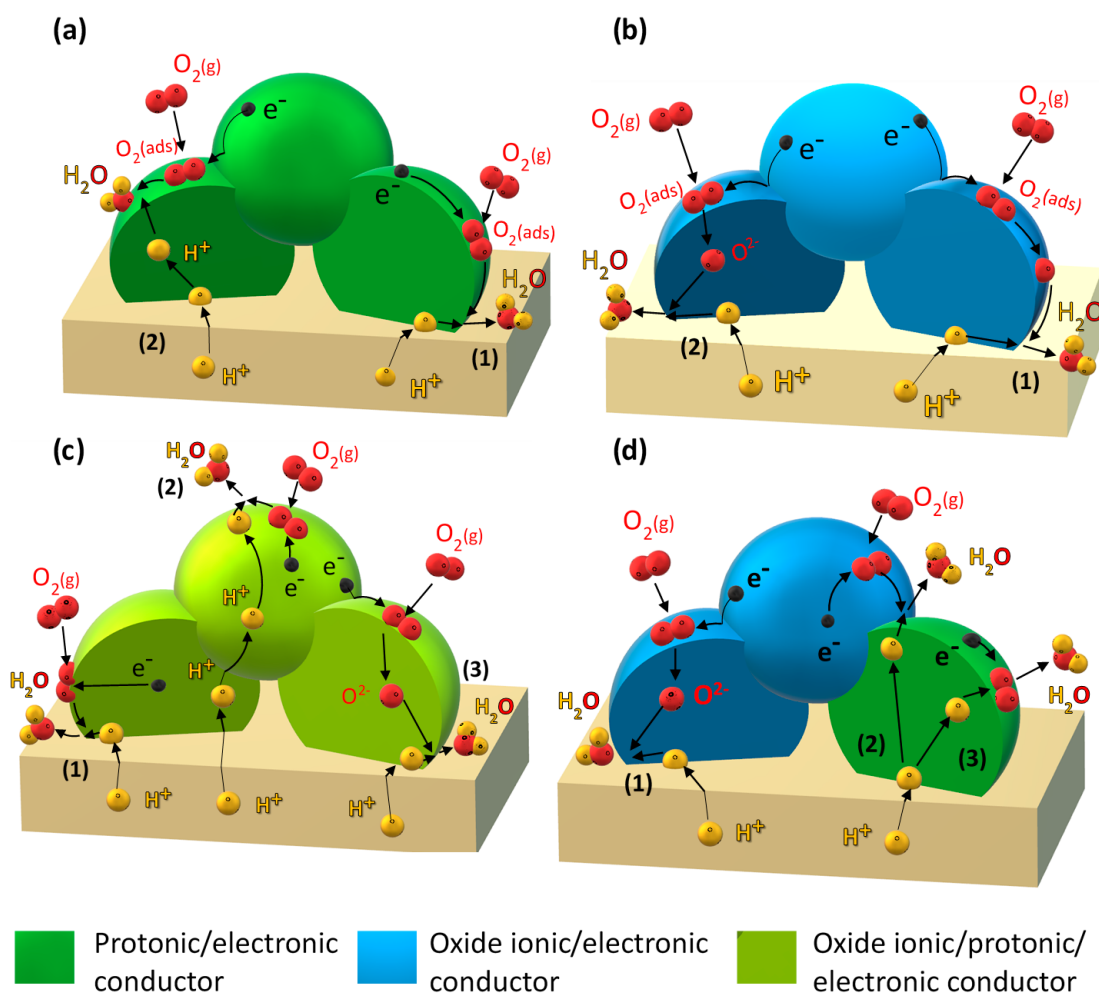


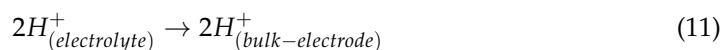
Figure 1. Electrochemical reaction steps corresponding to the cathodic reduction reaction occurring through: (a) the “electrode-surface path” (1) and “bulk-electrode path for protons” (2) for a mixed protonic–electronic conductor; (b) the “electrode-surface path” (1) and “bulk-electrode path for oxide ions” (2) for a mixed oxide-ion–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-ion–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 ion–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:



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 ($\text{H}_{(as)}^+$ 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:



High electronic conductivity is required in the cathode compartment not only for the reduction 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 $BaCe_{0.9-y}Pr_yGd_{0.1}O_{3-\delta}$ solid solution increases electron-hole conductivity, and a cathodic overpotential resistance of $0.47 \Omega \cdot cm^2$ is reported at $800^\circ C$ 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 $0.688 W \cdot cm^{-2}$ at $750^\circ C$ on a $BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BCZYb7111) electrolyte [25].

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

Composition	Abbreviation	Composition	Abbreviation
$BaCe_{0.8}Gd_{0.2}O_{2.9}$	BCG20	$Ce_{0.5}La_{0.5}O_{1.75}$	50LDC
$BaCe_{0.8}Sm_{0.2}O_{3-\delta}$	BCS20	$Ce_{0.8}Sm_{0.2}O_{2-\delta}$	20SDC
$BaCe_{0.9}Sm_{0.1}O_{3-\delta}$	BCS10	$GdBaCo_2O_{5+\delta}$	GBCO
$BaCe_{0.8}Y_{0.2}O_{3-\delta}$	BCY20	$LaCoO_{3-\delta}$	LCO
$BaCe_{0.85}Y_{0.15}O_{3-\delta}$	BCY15	$LaFeO_3$	LF
$BaCe_{0.9}Y_{0.1}O_{3-\delta}$	BCY10	$La_2NiO_{4\pm\delta}$	LNO
$BaCe_{0.9}Yb_{0.1}O_{3-\delta}$	BCYb10	$LaNi_{0.6}Fe_{0.4}O_{3-\delta}$	LNF
$BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-\delta}$	BCZY27	$La_{0.5}Sr_{0.5}CoO_{3-\delta}$	LSC55
$BaCe_{0.4}Zr_{0.4}Y_{0.2}O_{3-\delta}$	BCZY44	$La_{0.6}Sr_{0.4}CoO_{3-\delta}$	LSC64
$BaCe_{0.5}Zr_{0.3}Y_{0.2}O_{3-\delta}$	BCZY53	$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$	LSCF
$BaCe_{0.6}Zr_{0.2}Y_{0.2}O_{3-\delta}$	BCZY62	$La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$	LSCM
$BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-\delta}$	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
$BaCe_{0.4}Zr_{0.4}Y_{0.1}Yb_{0.1}O_{3-\delta}$	BCZYb4411	$La_{0.5}Sr_{0.5}MnO_{3-\delta}$	LSM55
$BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3-\delta}$	BCZYb7111	$La_{0.7}Sr_{0.3}MnO_{3-\delta}$	LSM73
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$	BSCF	$La_{0.8}Sr_{0.2}MnO_{3-\delta}$	LSM82
$BaZrO_{3-\delta}$	BZO	$NdBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$	NBSCF
$BaZr_{0.8}Y_{0.2}O_{3-\delta}$	BZY20	$PrBaCo_2O_{5+\delta}$	PBCO
$BaZr_{0.85}Y_{0.15}O_{3-\delta}$	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
$Ce_{0.9}Gd_{0.1}O_{2-\delta}$	10GDC	$Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$	SSC

For $BaZrO_3$ -based phases, co-doping strategies involving solid solutions, such as $BaZr_{0.8-x}Pr_xY_{0.2}O_{3-\delta}$ [26] and $BaZr_{0.9-x}Pr_xGd_{0.1}O_{3-\delta}$ [27], have been employed, and both 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 ($0.4 S \cdot cm^{-1}$ 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 $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZY20) as cathode material, reporting an electrode polarisation resistance (R_p) of $0.28 \Omega \cdot \text{cm}^2$ and a peak power density of $0.322 \text{ W} \cdot \text{cm}^{-2}$ at 700 °C for the composition $\text{BaZr}_{0.2}\text{Fe}_{0.6}\text{Y}_{0.2}\text{O}_{3-\delta}$ (Figure 2).

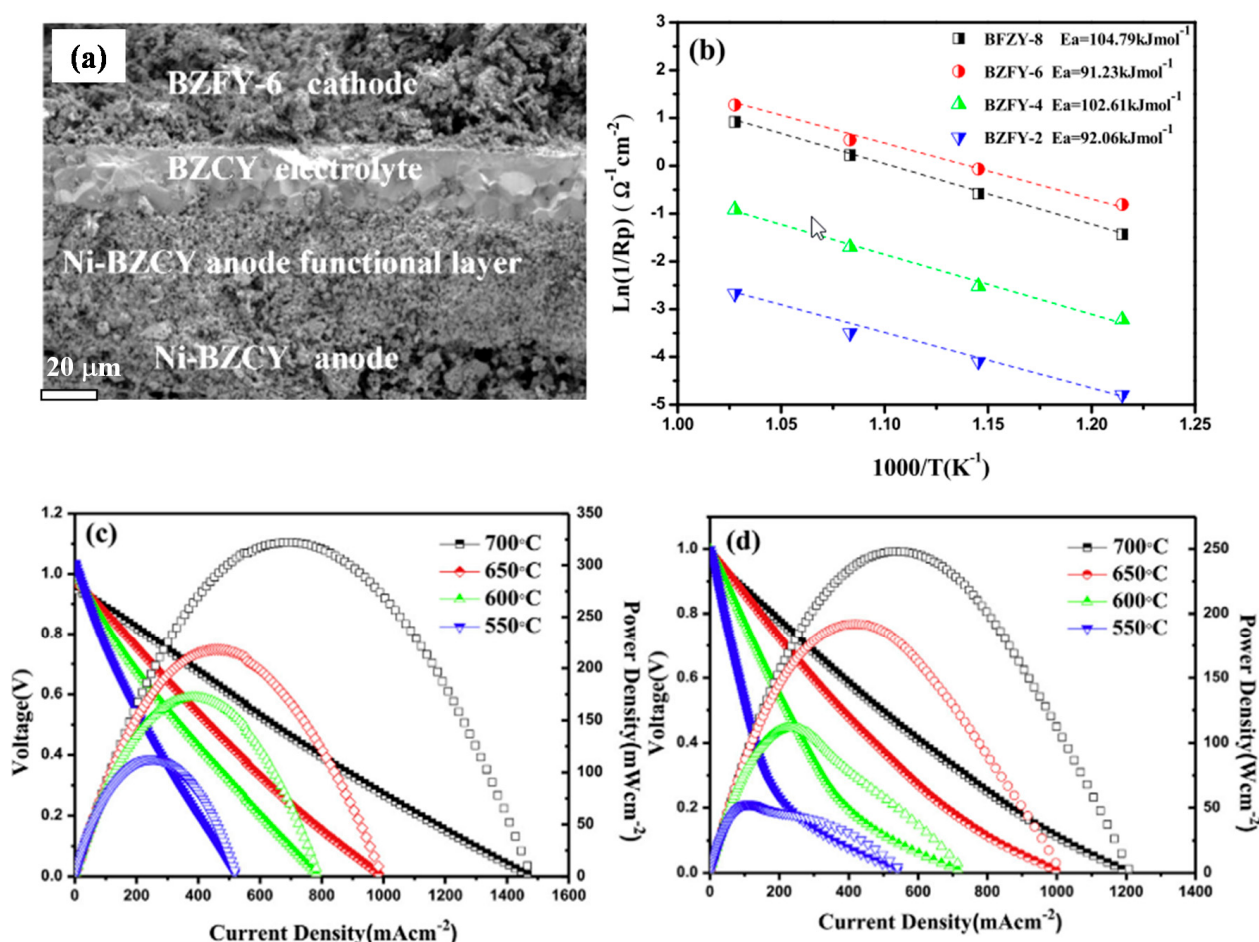


Figure 2. Microstructure of a $\text{BaZr}_{0.8-x}\text{Fe}_x\text{Y}_{0.2}\text{O}_{3-\delta}$ ($x = 0.6$) cathode over a $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_{3-\delta}$ electrolyte in an anode-supported cell (a); Arrhenius dependence of the electrode polarisation resistance for different Fe contents in the $\text{BaZr}_{0.8-x}\text{Fe}_x\text{Y}_{0.2}\text{O}_{3-\delta}$ series (b); current–voltage curves and current–power density curves for single cells with $\text{BaZr}_{0.2}\text{Fe}_{0.6}\text{Y}_{0.2}\text{O}_{3-\delta}$ (c) and $\text{BaFe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ cathodes (d). Copyright 2020 by Elsevier [32].

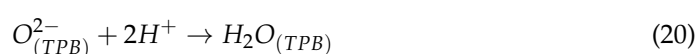
Fe doping in the $\text{BaCe}_{0.7-x}\text{Zr}_{0.2}\text{Y}_{0.1}\text{Fe}_x\text{O}_{3-\delta}$ series is reported to enhance transport properties ($R_p = 0.21 \Omega \cdot \text{cm}^2$ at 700 °C), but thermal expansion also increases substantially with increasing Fe content [33]. Cobalt is documented to have a moderate solid-solution limit in the series $\text{BaZr}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ but a promising electrode polarisation of $0.19 \Omega \cdot \text{cm}^2$ 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 $\text{BaCe}_{1-x}\text{Bi}_x\text{O}_{3-\delta}$ ($0 \leq x \leq 0.5$), 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, Solís 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:



Since the 1990s, there has been a general trend in SOFC research to replace Mn in the B site of the classical LaMnO₃-based perovskite cathode with Co and/or Fe [37]. The higher diffusion of oxide ions and faster kinetics at the electrode/electrolyte interface than LaMnO₃-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_{0.8}Sr_{0.2}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 $\text{Ba}(\text{Zr}_{0.5}\text{Ce}_{0.4})_{8/9}\text{Y}_{0.2}\text{O}_{3-\delta}$, reaching a hydrogen evolution rate of $127 \text{ mol}\cdot\text{cm}^{-2}\cdot\text{min}^{-1}$ at $0.5 \text{ A}\cdot\text{cm}^{-2}$ and 600°C [45].

Other authors have focused on Fe/Co-containing perovskites that are well known as SOFC cathodes, particularly $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF). Meng et al. [46] achieved a power density of $0.753 \text{ W}\cdot\text{cm}^{-2}$ at 700°C with LSCF on a $\text{BaCe}_{0.95}\text{Tb}_{0.05}\text{O}_{3-\delta}$ 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 $0.079\text{--}0.189 \text{ W}\cdot\text{cm}^{-2}$ in the temperature range $700\text{--}850^\circ\text{C}$ [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 BaCO_3 nanoparticles forming a synergistic catalyst, which reduced the polarisation resistance by nearly 75% from 1.123 to $0.293 \Omega\cdot\text{cm}^2$ at 700°C , yielding a power density of $0.404 \text{ W}\cdot\text{cm}^{-2}$ [49].

The well-known SOFC cathode $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) has also regularly been used and compared as a PCFC air electrode [50–52]. A very high power density of up to $0.800 \text{ W}\cdot\text{cm}^{-2}$ at 700°C , and a stable performance in CO_2 , with $\text{BaZr}_{0.4}\text{Ce}_{0.45}\text{Y}_{0.15}\text{O}_{3-\delta}$ as the electrolyte has been reported (Figure 3) [53].

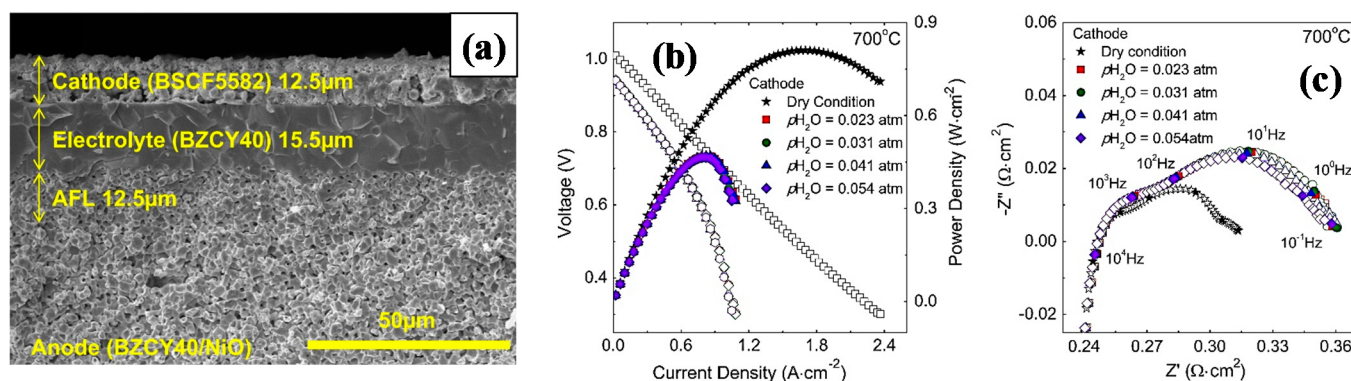


Figure 3. Microstructure of BSCF cathode on BZCY40 electrolyte (a), single-cell performance (b), and the corresponding Nyquist spectra at different water partial pressures (c). Copyright 2016 by Elsevier [53].

Dailly et al. compared the performance of BSCF, LSCF, and $\text{Pr}_2\text{NiO}_{4-\delta}$ (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 $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BCY10) electrolyte [51].

However, BSCF is reported to react with the LaNbO_4 -based electrolyte, whereas $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (LSCM) is chemically compatible with a lower ASR value for the electrode process [54]. Similar behavior was observed with the proton-conducting electrolyte $\text{La}_6\text{WO}_{12}$, which is stable with $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_{3-\delta}$ (LSM73) and LSCM but reacts with BSCF [55]. In 2013, Shang et al. [56] documented that the phase $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.2}\text{O}_{3-\delta}$ (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 $0.225 \text{ W}\cdot\text{cm}^{-2}$ at 600°C . Rare-earth doping in the related $\text{BaCo}_{0.4}\text{Fe}_{0.5-x}\text{Ce}_{0.1}\text{Re}_x\text{O}_{3-\delta}$ ($\text{Re} = \text{Y}, \text{Gd}; x = 0.1$) system has also been reported, with the Gd-doped phase exhibiting a promising peak power density of $0.504 \text{ W}\cdot\text{cm}^{-2}$ at 600°C in a cell with BCZYYb7111 as the electrolyte [57].

Tolchard et al. [58] assessed the reactivity of SOFC perovskite cathodes LaMO_3 ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}$) and the layered phase $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ ($x = 0, 0.8$) in contact with $\text{SrCeO}_{3-\delta}$ -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 $\text{La}_{1.2}\text{Sr}_{0.8}\text{NiO}_{4+\delta}$ does not react. The chemical compatibility of the same perovskite compositions with BaZrO_3 -based electrolytes was better, with only minor interdiffusion of Ba and La occurring [59]. Nevertheless, the authors

point out that thermal expansion mismatch should be controlled with careful choice of chemical substitutions.

The significant, deleterious effects of cobalt on stability in H_2O 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. $(\text{La,Sr})\text{FeO}_{3-\delta}$ has proved to be a popular choice as a Co-free cathode since Yamaura et al. [60] showed that the overpotential of $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_{3-\delta}$ was smaller than that of both $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_{3-\delta}$ and $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_{3-\delta}$ using $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$ as the electrolyte. Yuan et al. reported a power output of $0.538 \text{ W}\cdot\text{cm}^{-2}$ at 650°C on BCZY71 electrolyte using cobalt-free $\text{SrFe}_{0.95}\text{Nb}_{0.05}\text{O}_{3-\delta}$ as the cathode [61]. A further La-free electrode with good performance is $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{3-\delta}$ [62], with a power output of $0.486 \text{ W}\cdot\text{cm}^{-2}$ 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 $\text{Nd}_{0.5}\text{Ba}_{0.5}\text{Fe}_{0.9}\text{M}_{0.1}\text{O}_{3-\delta}$ ($\text{M} = \text{Ni, Cu, Co}$) indicates that the introduction of cobalt leads to higher ionic conductivity and lower polarisation resistance [63].

The $\text{RBa}(\text{Co,M})_4\text{O}_7$ series ($\text{R} = \text{Y, Ca}$; $\text{M} = \text{Zn, Fe, Al}$) with tetrahedral corner-sharing $(\text{Co/M})\text{O}_4$ 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 $\text{YBa}_3\text{Co}_3\text{ZnO}_7$ is most promising due to its high thermal stability [64]. $\text{Y}_{0.8}\text{Ca}_{0.2}\text{BaCo}_4\text{O}_7$ exhibits a good electrochemical performance on BCZY71 electrolyte, achieving a maximum power density (MPD) of $0.472 \text{ W}\cdot\text{cm}^{-2}$ at 700°C [65]. The same composition was deposited by a tape-calendering method on $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BCZY53) electrolyte, providing an MPD of $0.308 \text{ W}\cdot\text{cm}^{-2}$ 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 CdI_2 -type layer stacked along the c-direction, have been of interest due to their good thermoelectric properties [67]. The $\text{Ca}_{3-x}\text{La}_x\text{Co}_4\text{O}_{9+\delta}$ ($x = 0, 0.3$) series was reported to have high electrical conductivity ($53 \text{ S}\cdot\text{cm}^{-1}$ at 600°C , for $x = 0.3$) and promising electrocatalytic activity on BCY10 electrolyte [68]. The composition $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ was employed more recently in a reversible protonic ceramic cell based on a BCZY53 electrolyte, yielding a power density of $\approx 0.290 \text{ W}\cdot\text{cm}^{-2}$ in fuel-cell mode and an electrolysis current of $\approx 0.580 \text{ A}\cdot\text{cm}^{-2}$ 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 species 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 $\text{A}_2\text{B}_2\text{O}_{5+\delta}$ [70] or Ruddlesden–Popper (RP) perovskite-related structures of general formula $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$ [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 ($\text{CaTi}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$, and the RP series $\text{La}_2\text{NiO}_{4+\delta}$ and $\text{La}_4\text{Ni}_3\text{O}_{10}$) as electrodes for LaNbO_4 -based electrolyte thin films [76]. The layered RP-type cathode was then employed on BCY10 electrolyte, providing a power density of $0.130 \text{ W}\cdot\text{cm}^{-2}$ at 650°C [77]. Dailly et al. [78] studied a series of perovskite oxides $\text{AMO}_{3-\delta}$ ($\text{A} = \text{La, Ba, Sr}$; $\text{M} = \text{Mn, Fe, Co, Ni}$) and layered RP-type materials $\text{A}_2\text{MO}_{4+\delta}$ ($\text{A} = \text{La, Nd, Pr or Sr}$; $\text{M} = \text{Ni}$), noting that the lowest electrode polarisation resistances are observed for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ and $\text{Pr}_2\text{NiO}_{4+\delta}$. Dailly and Marrony then reported the successful operation of a single cell over 1000 h with an Nd_2NiO_4 layered cathode, although the power output was low ($0.060 \text{ W}\cdot\text{cm}^{-2}$ 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 LSCF, BSCF, $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) and $\text{La}_2\text{NiO}_{4+\delta}$ by TGA and polarisation studies, indicating that proton transfer and water release appear to be the rate-determining steps for BSCF, PBCO, and $\text{Pr}_2\text{NiO}_{4+\delta}$, but that no rate-determining step involving protons was found for LSCF. The same group also studied the effect of Sr content in the $\text{Pr}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ system on the oxygen reduction reaction and hydration, indicating that evidence for triple conduction exists in the $\text{Pr}_2\text{NiO}_{4+\delta}$ phase but not in the Sr-doped composition [81].

Ruddlesden–Popper nickelates of the form $\text{A}_2\text{NiO}_{4+\delta}$, and in particular the praseodymium analogue ($\text{Pr}_2\text{NiO}_{4+\delta}$), have continued to be the focus of study in protonic ceramic cells. A high performance of $0.82 \text{ W}\cdot\text{cm}^{-2}$ was recently obtained with a $\text{Pr}_2\text{NiO}_{4+\delta}$ cathode on $\text{BaCe}_{0.55}\text{Zr}_{0.3}\text{Y}_{0.15}\text{O}_{3-\delta}$ electrolyte at 650°C , employing a microwave heat treatment to minimize the reaction between the cathode and electrolyte [82]. In electrolysis mode, a $\text{Pr}_{1.95}\text{Ba}_{0.05}\text{NiO}_{4+\delta}$ oxygen electrode was reported to provide an excellent hydrogen production rate of $19 \text{ mL}\cdot\text{min}^{-1}$ at 600°C on a tubular $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Dy}_{0.2}\text{O}_{3-\delta}$ electrolyte [83]. Ba-doping in the nickelate series $\text{Nd}_{2-x}\text{Ba}_x\text{NiO}_{4+\delta}$ is documented to reduce diffusion of Ba from the electrolyte to the electrode [84], whereas anion doping with F in the series $\text{Nd}_{1.9}\text{Ba}_{0.1}\text{NiO}_{4+\delta}\text{F}_\gamma$ improves the electrochemical performance in electrolysis mode [85]. A single cell with $\text{La}_{1.2}\text{Sr}_{0.8}\text{Ni}_{0.6}\text{Fe}_{0.4}\text{O}_{4+\delta}$ (LSNF) cathode based on a BCZY71 electrolyte achieved a maximum power density of $0.781 \text{ W}\cdot\text{cm}^{-2}$ with a low interfacial polarisation resistance of $0.078 \Omega\cdot\text{cm}^2$ at 700°C , demonstrating high long-term stability [86]. Another elevated power output was recently reported for Ca-doped La_2NiO_4 , with a composition of $\text{La}_{1.5}\text{Ca}_{0.5}\text{NiO}_{4+\delta}$, offering an MPD of $0.923 \text{ W}\cdot\text{cm}^{-2}$ at 700°C [87]. The effect of Co-doping in RP-type cathodes based on $\text{La}_3\text{Ni}_2\text{O}_7$ 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 $\text{LaSrCo}_{1-x}\text{Fe}_x\text{O}_{4+\delta}$ 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 La_2NiO_4 and $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$ were obtained by an electrospinning technique and employed as a highly efficient cathode, reaching a power density of $0.551 \text{ W}\cdot\text{cm}^{-2}$ 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 $\text{Li}_{0.2}\text{Ni}_{0.79}\text{Co}_{0.2}\text{Zn}_{0.01}\text{O}_2$ [91]. Fan and Su [92] explored the electrode properties of an $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode on BCZY71 electrolyte, which rendered an MPD of $0.410 \text{ W}\cdot\text{cm}^{-2}$ 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 $\text{Pr}_2\text{NiO}_{4+\delta}$ [93].

The first reports of using double perovskites in protonic ceramic cells appear around the same period as the RP nickelate phases. In 2008, $\text{GdBaCo}_2\text{O}_{5+\delta}$ (GBCO) was employed on a BCZY71 electrolyte, reaching a power density of $0.266 \text{ W}\cdot\text{cm}^{-2}$ at 700°C [94]. The same authors subsequently achieved better performances of 0.382 and $0.533 \text{ W}\cdot\text{cm}^{-2}$ at 700°C on substituting Gd with Sm ($\text{SmBaCo}_2\text{O}_{5+\delta}$) [95] and then also partially substituting Ba with Sr ($\text{SmBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+\delta}$) [96], respectively. Early studies of double perovskites include that of Ling et al. [97], who compared the performance of $\text{LaBaCuMO}_{5+\delta}$ ($\text{M} = \text{Fe}, \text{Co}$) and similarly found that the better single-cell performance of the Co-containing phase ($0.432 \text{ W}\cdot\text{cm}^{-2}$ at 700°C), in comparison to the Fe-containing analogue ($0.327 \text{ W}\cdot\text{cm}^{-2}$ 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 $1.61 \text{ W}\cdot\text{cm}^{-2}$ at 750°C for a single cell with a BCZYYb7111 electrolyte and the layered double-perovskite cathode $\text{NdBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_{5+\delta}$ (NBSCF) [98]. Strandbakke et al. [99] studied a series of double perovskites $\text{BaGd}_{0.8}\text{La}_{0.2}\text{Co}_2\text{O}_{5+\delta}$, $\text{BaGdCo}_{1.8}\text{Fe}_{0.2}\text{O}_{5+\delta}$, $\text{PrBaCo}_2\text{O}_{5+\delta}$, and $\text{BaPrCo}_{1.4}\text{Fe}_{0.6}\text{O}_{5+\delta}$ 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]. Briec et al. [100] employed molecular dynamics to study proton diffusion in GBCO and found that the predominant mechanism was proton transfer between neighbouring oxygens (Gröthuss mechanism) but that vehicular migration via OH groups may also occur.

The praseodymium-containing analogue of NBSCF, $\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_{5+\delta}$ (PBSCF), was subsequently reported to proffer an exceptional power density ($0.500 \text{ W}\cdot\text{cm}^{-2}$ at 500°C) when employed as a dense interlayer between the electrolyte $\text{BaZr}_{0.4}\text{Ce}_{0.4}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BCZYYb4411) and a cathode of the same material [101]. In the same work, the authors offer evidence of proton uptake in PBSCF by TGA and attribute the very low contact resistance between the electrolyte and cathode to the proton permeability of the dense PBSCF interlayer.

The same group then demonstrated reversible operation of the $\text{NiO-BCZYYb4411/PBSCF}$ cell, which showed negligible degradation after 500 h of operation at 550°C with a current density of $-1.80 \text{ A}\cdot\text{cm}^{-2}$ 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 $\text{BaCe}_{0.6}\text{Zr}_{0.2}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ anode support, reaching an MPD of $0.250\text{--}0.650 \text{ W}\cdot\text{cm}^{-2}$ at $500\text{--}600^\circ\text{C}$ [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 $\text{LaBaCo}_2\text{O}_{5+\delta}$ and -disordered $\text{La}_{0.5}\text{Ba}_{0.5}\text{Co}_2\text{O}_{5+\delta}$ 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 $\text{LaBaCo}_2\text{O}_{5+\delta}$ compared to the disordered phase. An A-site-deficient, layered perovskite, $(\text{PrBa}_{0.8}\text{Ca}_{0.2})_{0.95}\text{Co}_2\text{O}_{6-\delta}$, was developed as an oxygen electrode for a reversible protonic ceramic cell where current density reached $-0.72 \text{ A}\cdot\text{cm}^{-2}$ at 1.3 V , and a peak power density of $0.540 \text{ W}\cdot\text{cm}^{-2}$ 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, $\text{Sr}_2\text{Sc}_{0.1}\text{Nb}_{0.1}\text{Co}_{1.5}\text{Fe}_{0.3}\text{O}_{6-\delta}$ (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, $0.840 \text{ W}\cdot\text{cm}^{-2}$ at 650°C on BCZYYb7111 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 $\text{GdBaCuCoO}_{5+\delta}$ on a BCZY71 electrolyte with a power density of $0.480 \text{ W}\cdot\text{cm}^{-2}$ 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 $\text{Pr}_2\text{BaNiMnO}_{7-\delta}$ cathode that showed excellent compatibility with BCZYYb7111 electrolyte and generated a remarkable MPD of $1.07 \text{ W}\cdot\text{cm}^{-2}$ at 700°C with almost negligible degradation after 100 h.

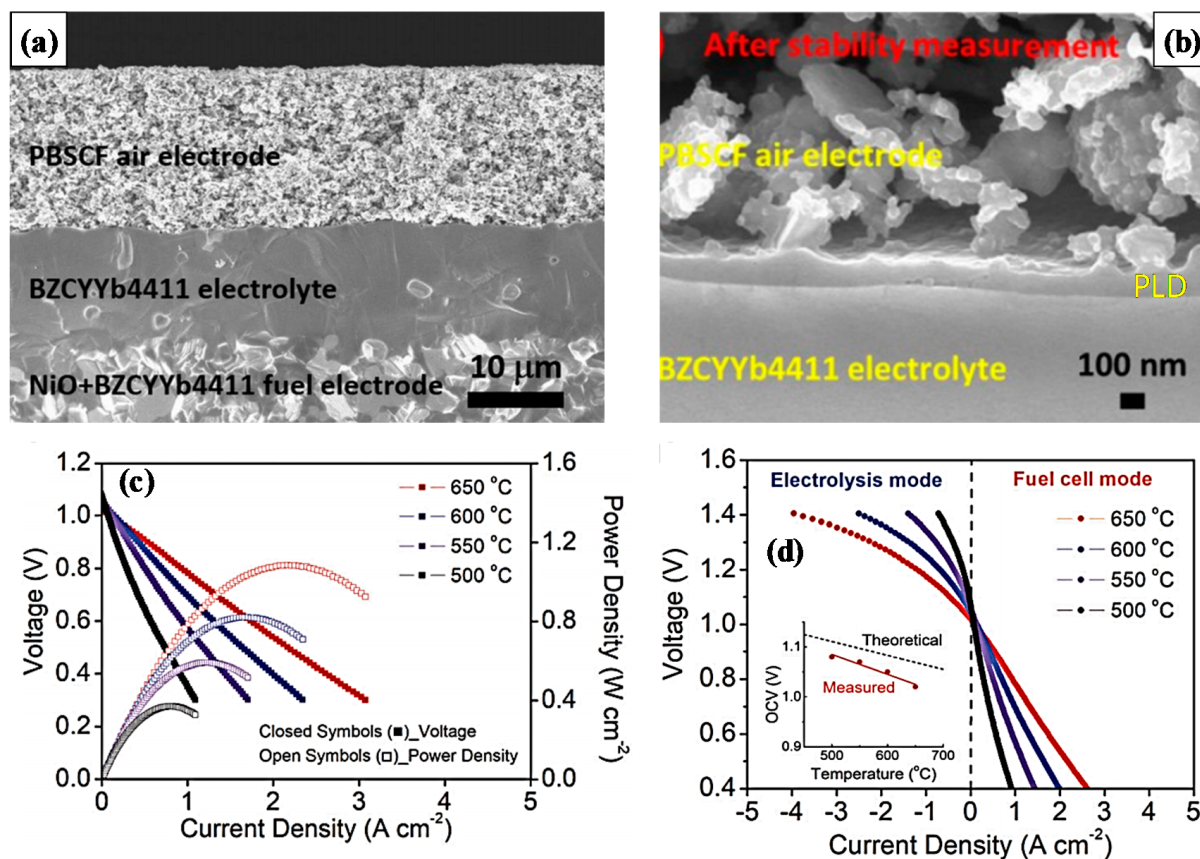


Figure 4. SEM cross-section images of a single cell based on a PBSCF cathode on BZCYYb4411 electrolyte (a); magnification image corresponding to PBSCF interlayer deposited by pulsed laser deposition (PLD); (b) electrochemical performance of the single cell at different temperatures (c); and polarization curves in both electrolysis and fuel cell modes (d). Copyright 2019 by Royal Society of Chemistry [102].

The origin of triple conduction in the double perovskites has been the focus of several studies. EIS as a function of $p\text{O}_2$ and $p\text{H}_2\text{O}$ was employed to indicate that, for $\text{PrBaCo}_2\text{O}_{5+\delta}$, 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 ^2H 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. ^2H 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

$\text{Gd}_{0.8}\text{La}_{0.2}\text{Ba}_{0.95}\text{La}_{0.05}\text{Co}_2\text{O}_{6-\delta}$ does not hydrate, the impurity phase $\text{BaCo}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$ 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 $\text{BaGd}_{0.8}\text{La}_{0.2}\text{Co}_2\text{O}_{6-\delta}$ (BGLC) incorporates protons in the bulk, whereas the simple perovskite $\text{Ba}_{0.5}\text{La}_{0.5}\text{CoO}_{3-\delta}$ (BLC) does not [112]. Nevertheless, a better performance as electrolyser with a $\text{SrZr}_{0.5}\text{Ce}_{0.4}\text{Y}_{0.1}\text{O}_{3-\delta}$ electrolyte was observed for BLC. A recent study also adopts the double perovskite $\text{Ba}_{1-x}\text{Gd}_{0.8}\text{La}_{0.2+x}\text{Co}_2\text{O}_{6-\delta}$ as the steam anode in a tubular protonic ceramic electrolysis cell with a low polarisation resistance ($<1\ \Omega\cdot\text{cm}^2$) at $600\ ^\circ\text{C}$ [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 $\text{BaCo}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$.

Recently, a simple cobaltite perovskite $\text{PrNi}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$ (PNC) associated with triple-conducting properties was processed with a nanofibre microstructure, leading to a very low polarisation resistance of $0.055\ \Omega\cdot\text{cm}^2$ at $500\ ^\circ\text{C}$ and an excellent MPD of $0.611\ \text{W}\cdot\text{cm}^{-2}$ at $600\ ^\circ\text{C}$ when operating on BCZYb4411 electrolyte [114] (Figure 5).

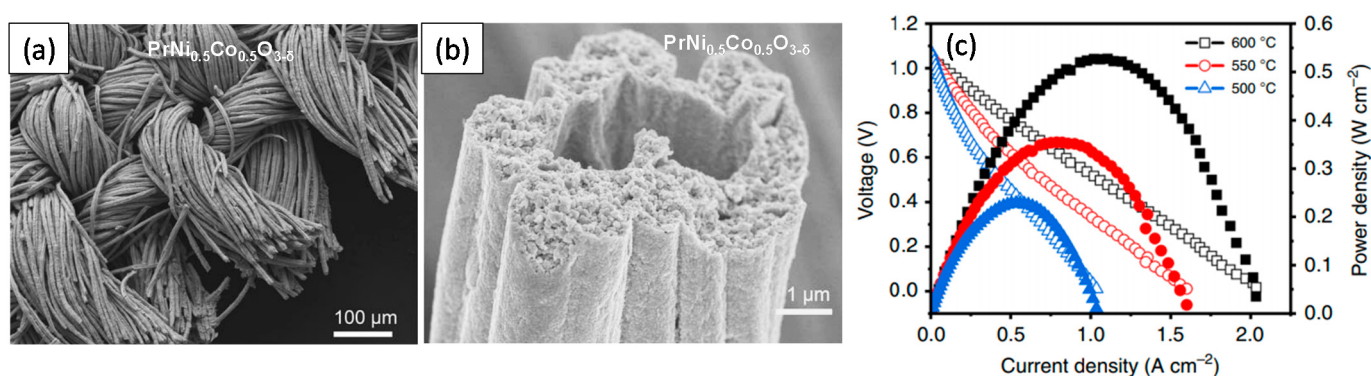


Figure 5. (a) SEM image of a nanofibre-structured $\text{PrNi}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$ electrode; (b) magnified image of corresponding hollow fibre; (c) single-cell performance of the PNC cathode over a BCZYb4411 electrolyte and Ni-BCZYb4411 anode in the range $500\text{--}600\ ^\circ\text{C}$. Copyright 2020 by Springer Nature [114].

Another simple cobaltite perovskite developed in 2014, around the period that the first double perovskites were reported, is $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BCFZY). This phase gave an excellent power output of $0.455\ \text{W}\cdot\text{cm}^{-2}$ at $500\ ^\circ\text{C}$ due to its triple-conducting character [115]. The same material then demonstrated excellent performance as a cathode in SOFCs with an oxide-ion conducting $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ 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 $0.797\ \text{W}\cdot\text{cm}^{-2}$ was achieved at $650\ ^\circ\text{C}$ for the composition $\text{Ba}_{0.9}\text{Co}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$ [118]. B-site deficiency in BCFZY is also reported to enhance performance with a cell containing a $\text{Ba}(\text{Co}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1})_{0.95}\text{O}_{3-\delta}$ cathode, achieving a power output of $0.840\ \text{W}\cdot\text{cm}^{-2}$ at $650\ ^\circ\text{C}$ on a thin-film, B-site-deficient $\text{Ba}(\text{Zr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1})_{0.95}\text{O}_{3-\delta}$ electrolyte [119]. On partially replacing Ba by Ca to obtain $\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Co}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$, Li et al. [120] reduced superficial Ba segregation, improving phase stability and CO_2 tolerance, as well as the electrocatalytic performance. Recently, Ni-doped $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$ was also evaluated with a $\text{Ba}(\text{Ce}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.1}\text{Yb}_{0.1})_{0.95}\text{O}_{3-\delta}$ electrolyte, showing improved oxygen mobility, bulk oxide-ion-proton conductivity, and surface exchange kinetics [121].

BCFZY is arrived at through Y-doping of the $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.2}\text{O}_{3-\delta}$ 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

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 $(\text{Ba}, \text{Sr}, \text{La})(\text{Fe}, \text{Co}, \text{Zn}, \text{Y})\text{O}_{3-\delta}$, finding that proton uptake is greatest with Zn on the B-site, while Co has the opposite effect [123]. The Co-free composition $\text{Ba}_{0.95}\text{La}_{0.05}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{3-\delta}$ 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 $\text{BaFeO}_{3-\delta}$ [125]. The cobalt-free composition $\text{BaFe}_{0.5}\text{Sn}_{0.2}\text{Bi}_{0.3}\text{O}_{3-\delta}$ reached an MPD of $1.28 \text{ W}\cdot\text{cm}^{-2}$ 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 $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$, 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 SSC and the proton conductor $\text{BaCe}_{0.8}\text{Sm}_{0.2}\text{O}_{3-\delta}$ (BCS20) [127]. The interfacial R_p reached a minimum for approximately 60 wt % SSC ($0.21 \Omega\cdot\text{cm}^2$ at 700°C and MPD of $0.24 \text{ W}\cdot\text{cm}^{-2}$). SSC was then adopted with the more stable proton conductor, rendering an MPD of $0.528 \text{ W}\cdot\text{cm}^{-2}$ at 700°C with $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.16}\text{Zn}_{0.04}\text{O}_{3-\delta}$ also as electrolyte [128]. Dailly et al. achieve a very similar MPD, $0.529 \text{ W}\cdot\text{cm}^{-2}$ at 700°C , employing an SSC- $\text{BaCe}_{0.8}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BCZY81) composite cathode deposited on BZCY81 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 $0.3 \text{ W}\cdot\text{cm}^{-2}$ at 600°C [130]. By preparing a fibrous composite cathode of SSC with embedded $\text{BaCe}_{0.5}\text{Zr}_{0.35}\text{Y}_{0.15}\text{O}_{3-\delta}$ particles using an electrospinning process, Park et al. achieved a lower polarisation resistance of $0.185 \Omega\cdot\text{cm}^2$ at 700°C in comparison to a typical nanocomposite electrode (MPD was $0.64 \text{ W}\cdot\text{cm}^{-2}$ 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 $0.6 \text{ W}\cdot\text{cm}^{-2}$ 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 pO_2 and pH_2O [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 O_{ad} to O_{ad}^- and surface diffusion of O_{ad}^- . 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- $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (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 $SrCo_{0.8}Fe_{0.15}Zr_{0.05}O_{3-\delta}$ -BCZYYb7111 composite cathode with high structural stability and CO_2 tolerance, which exhibited a low R_p value of $0.07 \Omega \cdot cm^2$ at $700^\circ C$ and an MPD of $0.71 W \cdot cm^{-2}$ at $700^\circ C$. A composite cathode composed of a single and a layered perovskite, $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ - $SmBaCo_2O_{5+\delta}$, has recently been reported, showing a low R_p ($0.18 \Omega \cdot cm^2$ at $700^\circ C$) and a remarkable MPD of $1.57 W \cdot cm^{-2}$ at $750^\circ C$ [137].

Other perovskite cobaltites employed as the MIEC phase in a composite electrode include $LaCoO_3$, which was infiltrated into a porous BZCY712 backbone, thereby avoiding detrimental cation interdiffusion, which may occur on high-temperature sintering; a low R_p of $0.11 \Omega \cdot cm^2$ at $600^\circ C$ in air was attained [138]. A barium lanthanide cobaltite, $Ba_4Sr_2Sm_2Co_4O_{15}$, was used in a composite cathode with $BaCe_{0.5}Pr_{0.3}Y_{0.2}O_{3-\delta}$ proton conductor, achieving the best performance for a 30:70 wt % $Ba_4Sr_2Sm_2Co_4O_{15}$ / $BaCe_{0.5}Pr_{0.3}Y_{0.2}O_{3-\delta}$ ratio, with $Ba_4Sr_2Sm_2Co_4O_{15}$ serving as an active phase for the dissociative absorption of oxygen; an MPD of $0.197 W \cdot cm^{-2}$ at $600^\circ C$ and stability of $Ba_4Sr_2Sm_2Co_4O_{15}$ in 1% CO_2 in air was reported [139]. The cobaltite composite $La_{0.5}Ba_{0.5}CoO_{3-\delta}$ - $BaZrO_3$ was prepared by both a modified Pechini method, followed by exsolution from the previously prepared, single-phase perovskite $La_{0.3}Ba_{0.7}Zr_{0.4}Co_{0.6}O_{3-\delta}$, and by direct calcination of the precursor, with the former process demonstrating an R_p of $1.54 \Omega \cdot cm^2$ at $600^\circ C$ [140]. A similar synthesis technique was then employed for the fabrication of $La_{1-x}Ba_xCoO_{3-\delta}$ - $BaZr_{0.9}Y_{0.1}O_{2.95}$ electrodes with direct deposition of the single-phase precursor material on the $BaZr_{0.9}Y_{0.1}O_{3-\delta}$ (BZY10) electrolyte [141]; weight ratios of $La_{1-x}Ba_xCoO_{3-\delta}$:BZY10 of 60:40 and 80:20 were associated with R_p values of 0.21 and $0.27 \Omega \cdot cm^2$ at $600^\circ C$, respectively. The cobaltite perovskite $SrCo_{0.7}Fe_{0.2}Zr_{0.1}O_{3-\delta}$ (SCFZ) 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 $0.129 W \cdot cm^{-2}$ and 91% selective ethylene yield at 21% ethane conversion at $700^\circ C$ [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- $BaCe_{0.9}Yb_{0.1}O_{3-\delta}$ (BCYb10) cathodes in a ratio of 50:50 wt % with an R_p of $0.14 \Omega \cdot cm^2$ at $700^\circ C$, 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 pO_2 and pH_2O , 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, $BaCe_{0.5}Zr_{0.35}Y_{0.15}O_{3-\delta}$ -embedded LSCF fibrous cathodes were prepared using an LSCF precursor gel containing the $BaCe_{0.5}Zr_{0.35}Y_{0.15}O_{3-\delta}$ nanopowder; an anode-supported single cell of this cathode on $BaCe_{0.5}Zr_{0.35}Y_{0.15}O_{3-\delta}$ electrolyte provided an MPD of $0.537 W \cdot cm^{-2}$ at $700^\circ C$ [145]. The mixed cobaltite-ferrite series $Ca_xY_{1-x}Fe_{0.5}Co_{0.5}O_{3-\delta}$ exhibits high conductivities ($202 S \cdot cm^{-1}$ at $750^\circ C$ for $x = 0.3$) and excellent compatibility with BCZY71 electrolyte [146] (Figure 6). The power density produced by a $Ca_{0.3}Y_{0.7}Fe_{0.5}Co_{0.5}O_{3-\delta}$ -BCZY71 composite cathode on BCZY71 electrolyte was $0.798 W \cdot cm^{-2}$ at $750^\circ C$ [146].

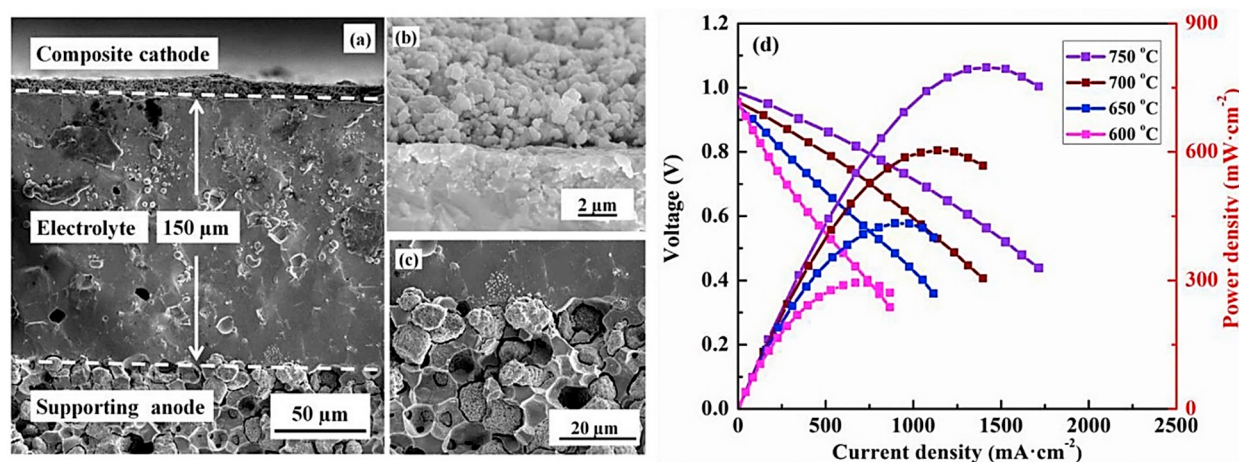


Figure 6. SEM images of (a) a protonic ceramic fuel cell based on a $\text{Ca}_{0.3}\text{Y}_{0.7}\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$ -BCZY71 composite cathode over BCZY71 electrolyte, (b) cathode-electrolyte interface, and (c) anode-electrolyte interface; (d) performance of the single cell at different temperatures. Copyright 2019 by Elsevier [146].

Shimada et al. [147] undertook a performance comparison of cobaltite perovskite electrodes $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSC64), $\text{La}_{0.6}\text{Ba}_{0.4}\text{CoO}_{3-\delta}$, 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 $\text{La}_{0.6}\text{Ba}_{0.4}\text{CoO}_{3-\delta}$ -BCZYYb7111 composite achieving the best power output ($1.0 \text{ W}\cdot\text{cm}^{-2}$ 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 $0.42 \text{ W}\cdot\text{cm}^{-2}$ and a low R_p of $0.1 \Omega\cdot\text{cm}^2$ at 700°C with a BCZY71 electrolyte [148]. Taillades et al. [149] then showed that a composite BSCF-BCY10 exhibited a lower ASR value ($0.53 \Omega\cdot\text{cm}^2$ at 600°C) compared to pure BSCF. The same group subsequently fabricated a BSCF-BZCYYb1711 cathode deposited on a BCZYYb7111 electrolyte by wet powder spraying, achieving an MPD of $0.422 \text{ W}\cdot\text{cm}^{-2}$ at 600°C [150]. A reversible protonic ceramic cell was developed by Marrony and Dailly [151] employing a BCZY81-ZnO (5 mol%) electrolyte and BSCF-BCZY81 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, $\text{Ba}_{0.4}\text{K}_{0.1}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, exhibited a lower proton migration energy when compared with undoped-BSCF [152]. The composite $\text{Ba}_{0.4}\text{K}_{0.1}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ -BCZY71 provided an exceptionally high MPD of $1.275 \text{ W}\cdot\text{cm}^2$ 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 $0.018 \Omega\cdot\text{cm}^2$ 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 $\text{BaCe}_{0.8}\text{Sm}_{0.2}\text{O}_{3-\delta}$ and $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_{3-\delta}$ (LSF73) on a $\text{BaCe}_{0.8}\text{Sm}_{0.2}\text{O}_{3-\delta}$ electrolyte, generating an MPD of $0.35 \text{ W}\cdot\text{cm}^{-2}$ 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 $(\text{La}_{0.7}\text{Sr}_{0.3})\text{V}_{0.9}\text{O}_{3-\delta}$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$, respectively, into the proton conductor $\text{BaCe}_{0.51}\text{Zr}_{0.3}\text{Y}_{0.15}\text{Zn}_{0.04}\text{O}_{3-\delta}$ as scaffold, and the cell performance was compared to that of YSZ and $\text{Ba}(\text{Ce}_{0.51}\text{Zr}_{0.30}\text{Y}_{0.15}\text{Zn}_{0.04})\text{O}_{3-\delta}$ 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 $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ (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 $\text{BaZr}_{0.75}\text{Y}_{0.15}\text{O}_{3-\delta}$, $\text{BaCe}_{0.75}\text{Y}_{0.15}\text{O}_{3-\delta}$, and $\text{BaCe}_{0.45}\text{Zr}_{0.30}\text{Y}_{0.15}\text{O}_{3-\delta}$ scaffolds infiltrated with LSF found the best cathode performance for the $\text{BaZr}_{0.75}\text{Y}_{0.15}\text{O}_{3-\delta}$ and $\text{BaCe}_{0.45}\text{Zr}_{0.30}\text{Y}_{0.15}\text{O}_{3-\delta}$ scaffolds. Ren et al. [159] studied the influence of Zr^{4+} doping on the $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ perovskite, achieving improved proton diffusion kinetics, $D_{\text{H,Chem}} = 8.71 \cdot 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, and a low polarisation resistance, $0.169 \Omega\cdot\text{cm}^2$ (both at 700°C) for Zr-doped material. Recently, Lei et al. [160] reported a nanostructured $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ composite cathode operating in electrolyser mode, with a performance of $0.21 \text{ A}\cdot\text{cm}^{-2}$ at 600°C and a faradaic 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_2O as catalyst significantly improves the cathodic performance in the range $400\text{--}600^\circ\text{C}$. 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 $0.45 \text{ W}\cdot\text{cm}^{-2}$ at 700°C . The same group then optimised the LSF73-20SDC cathode in terms of microstructure and electrolyte-interface characteristics, raising the MPD to $0.542 \text{ W}\cdot\text{cm}^{-2}$ at 650°C [163]. The proton-blocking strategy is further explored with the composite $\text{La}_2\text{NiO}_{4+\delta}$ - $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$ electrode, with a 70:30 wt % mixture showing the lowest ASR and an MPD of $0.590 \text{ W}\cdot\text{cm}^{-2}$ at 700°C on BCZY71 electrolyte [164]. Another ferrite-based, cobalt-free, composite cathode achieving a high power output is $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ -20SDC with MPD values of 0.45 and $0.55 \text{ W}\cdot\text{cm}^{-2}$ at 650°C on $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.2}\text{O}_{3-\delta}$ and BCZY71 electrolytes, respectively [165]. Further improvement was obtained on using $\text{La}_{0.35}\text{Pr}_{0.15}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ in the composite cathode, reaching a power density of $1.08 \text{ W}\cdot\text{cm}^{-2}$ at 700°C [166]. Vert et al. [167] studied the ferrite phase $\text{Pr}_{0.58}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ in conjunction with BCYb10, reporting the lowest polarisation resistance for a 50:50 vol % mixture. In the series of ferrite-based perovskites $\text{Nd}_{0.5}\text{Ba}_{0.5}\text{Fe}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ ($0 \leq x \leq 0.15$), the highest conductivity is observed for the $x = 0.1$ member [168]. A composite cathode of $\text{Nd}_{0.5}\text{Ba}_{0.5}\text{Fe}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ -BCZY71 on BCZY71 electrolyte exhibited a power density of $0.49 \text{ W}\cdot\text{cm}^{-2}$ at 700°C . The perovskite $\text{BaCe}_{0.4}\text{Fe}_{0.4}\text{Co}_{0.2}\text{O}_{3-\delta}$ 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 BZCYb17 electrolyte produced an MPD of $0.335 \text{ W}\cdot\text{cm}^{-2}$ at 700°C . A similar performance of $0.341 \text{ W}\cdot\text{cm}^{-2}$ and a low R_p of $0.1 \Omega\cdot\text{cm}^2$ at 700°C was achieved for the cobalt-free composite $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ -BCZY71 on BCZY71 electrolyte [170]. One of the best performances of a ferrite-based cobalt-free electrode was reported for the series $\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Fe}_{0.9-x}\text{Sn}_x\text{Y}_{0.1}\text{O}_{3-\delta}$ 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 $0.95 \text{ W}\cdot\text{cm}^{-2}$ at 700°C on

BCZY71 electrolyte [171]. Liu et al. [172] have recently reported on the ferrite-based series $(\text{SrBa})_{1-x}\text{Pr}_x(\text{CuTi})_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$, in which the best electrochemical performance is obtained for $x = 0.4$ in a composite with SDC, achieving an MPD of $0.925 \text{ W}\cdot\text{cm}^{-2}$ 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 $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ – $\text{La}_{0.5}\text{Ce}_{0.5}\text{O}_{1.75}$ (LSM82-50LDC) composite on an $\text{La}_{0.99}\text{Ca}_{0.01}\text{NbO}_4$ thin electrolyte, and report an MPD of $0.065 \text{ W}\cdot\text{cm}^{-2}$ 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 polarisation resistance. For composite electrodes with LSM82 and LaNbO_4 , the lowest electrode polarisation-resistance value ($R_p = 22 \Omega\cdot\text{cm}^2$ at 750°C) was achieved on mixing LSM82 and $\text{La}_{0.995}\text{Ca}_{0.005}\text{NbO}_4$ in a 50:50 vol % ratio. Solís 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 $\text{La}_{5.5}\text{WO}_{12-\delta}$ 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– $\text{La}_{5.5}\text{WO}_{11.25-\delta}$ 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– $\text{La}_{28-x}\text{W}_{4+x}\text{O}_{54+3x/2}$ ($x = 0.85$) could be accelerated on the addition of Pt nanoparticles [177].

Lee et al. [178] studied the effects of humidification on $\text{BaCe}_{0.85}\text{Y}_{0.15}\text{O}_{3-\delta}$ (BCY15)-based cells with LSM82– $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$ (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 $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_{3-\delta}$ (LSM55)-based cathode in conjunction with K_2NiF_4 -type layered $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_{4+\delta}$ 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 $0.94 \text{ W}\cdot\text{cm}^{-2}$ 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_6O_{11} – CeO_2 , lowered the R_p toward water splitting and oxygen evolution [180]. A similar composition, $(\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{Mn}_{0.5}\text{Cr}_{0.5}\text{O}_{3-\delta}$ – $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.16}\text{Zn}_{0.04}\text{O}_{3-\delta}$, 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 $\text{Nd}_{1.95}\text{NiO}_{4+\delta}$ and BCZYYb7111, with the lowest R_p observed for 60 wt % of the nickelate at $0.43 \Omega\cdot\text{cm}^2$ at 750°C and a power density of $0.154 \text{ W}\cdot\text{cm}^{-2}$ [182]; the relatively low MPD is attributed to a high electrolyte resistance. Babiniec et al. [183] made use of a thick, porous BCZY71 backbone, which was infiltrated with $\text{La}_2\text{NiO}_{4+\delta}$ nanoparticles for hydrogen-flux measurements. Similarly, nanoparticles of $(\text{Pr}_{0.9}\text{La}_{0.1})_2(\text{Ni}_{0.74}\text{Cu}_{0.21}\text{Nb}_{0.05})\text{O}_{4+\delta}$ were infiltrated on the surface of a BCZY71 skeleton with a load of 46 wt % to achieve an MPD of $0.770 \text{ W}\cdot\text{cm}^{-2}$ at 700°C ; the cell was operated without degradation for 200 h at 600°C [184] (Figure 7).

Tarutin et al. [185] employed a $\text{Pr}_{1.9}\text{Ba}_{0.1}\text{NiO}_{4+\delta}$ – $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Dy}_{0.2}\text{O}_{3-\delta}$ composite cathode, which was deposited by tape calendaring and co-sintered in a single step with $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Dy}_{0.2}\text{O}_{3-\delta}$ electrolyte and Ni – $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Dy}_{0.2}\text{O}_{3-\delta}$ anode layers; cell performance was reported as $0.470 \text{ W}\cdot\text{cm}^{-2}$ at 600°C . A similar composite of Pr_2NiO_4 –BCZY62 was used in electrolysis mode in a thin film BCZY62-based single cell, achieving a current density of $0.977 \text{ A}\cdot\text{cm}^{-2}$ at an electrolysis potential of 1.3 V [186] (Figure 8).

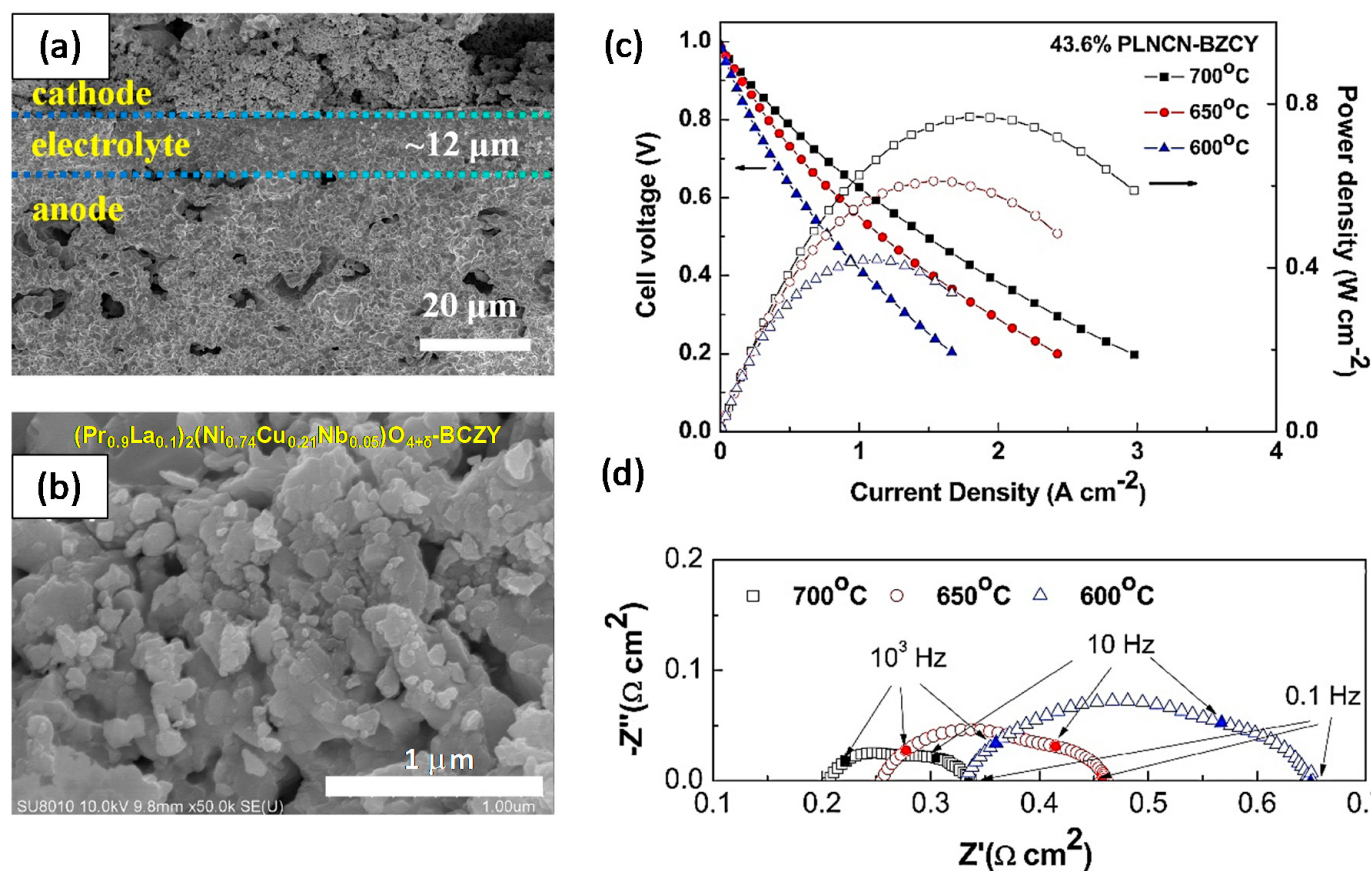


Figure 7. Scanning electron micrograph of a protonic ceramic single cell based on nanoparticles of $(\text{Pr}_{0.9}\text{La}_{0.1})_2(\text{Ni}_{0.74}\text{Cu}_{0.21}\text{Nb}_{0.05})\text{O}_{4+\delta}$ infiltrated on a BCZY71 skeleton as cathode, a BCZY71 electrolyte, and Ni-BCZY71 anode (a); magnified image of the cathode composite based on infiltrated nanoparticles on BCZY71 (b); single-cell performance curves (c) and impedance spectra of the cell under open circuit conditions (d), under humidified hydrogen and air in the range 600–700 °C. Copyright 2017 by Elsevier [184].

$\text{La}_2\text{NiO}_{4+\delta}$ has also been used as the scaffold for infiltration with $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$ (LNF) particles, with the cathode achieving an outstanding power output of $0.969 \text{ W}\cdot\text{cm}^{-2}$ at 700 °C employing an LNF loading of 31 wt % and a BCZY71 electrolyte [187]. Recently, Pikalova et al. [188] obtained an MPD of $0.17 \text{ W}\cdot\text{cm}^{-2}$ in $\text{Pr}_{1.7}\text{Ca}_{0.3}\text{NiO}_{4+\delta}$ composite cathodes with $\text{BaCe}_{0.8}\text{Gd}_{0.19}\text{Cu}_{0.01}\text{O}_{3-\delta}$ 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 $\text{SrEu}_2\text{Fe}_{1.8}\text{Co}_{0.2}\text{O}_{7-\delta}$ and BCZY71 as 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 $0.562 \text{ W}\cdot\text{cm}^{-2}$ 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 $\text{A}'\text{A}''\text{B}'\text{B}''\text{O}_{5+\delta}$. In a study aimed at improving the durability of PCFCs, Park et al. [190] employed a composite cathode of $\text{NdBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_{5+\delta}$ - $\text{Ce}_{0.9}\text{Nd}_{0.1}\text{O}_{2-\delta}$ with a BCZYYb7111 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 $p\text{O}_2$ and $p\text{H}_2\text{O}$ producing undesirable oxide phases on the cathode surface (Figure 9).

$\text{Nd}(\text{Ba}_{0.75}\text{Ca}_{0.25})\text{Co}_{1.5}\text{Fe}_{0.4}\text{Ni}_{0.1}\text{O}_{5+\delta}$ was prepared as a composite with both BCZYYb7111 and $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$ in the weight ratio 6:4, with the latter composite providing the better performance with a peak power density of $0.88 \text{ W}\cdot\text{cm}^{-2}$ on an anode-supported cell with

BCZYYb7111 electrolyte [191]. Additionally, $\text{NdBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_{5+\delta}$ was studied as an electrode in an electrolyser based on BCZYYb7111, reaching $3.16 \text{ A}\cdot\text{cm}^{-2}$ at 1.3 V and 750°C in H_2 [192].

The composite $\text{PrBaCo}_2\text{O}_{5+\delta}$ -BCZYYb7111 was prepared by impregnating a BCZYYb7111 scaffold with $\text{PrBaCo}_2\text{O}_{5+\delta}$ over five cycles. The optimal PBCO loading was ascertained at 36 wt % PBCO, leading to an MPD of $0.49 \text{ W}\cdot\text{cm}^{-2}$ at 750°C [193]. Ta-doped $\text{PrBaCo}_2\text{O}_{5+\delta}$ cathodes showed improved chemical stability and higher resistance to CO_2 [194]. In addition, composite cathodes of $\text{PrBa}_{0.9}\text{Ca}_{0.1}\text{Co}_{2-x}\text{Zn}_x\text{O}_{5+\delta}$ 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 $0.87 \text{ W}\cdot\text{cm}^{-2}$ for the $x = 0.15$ composition at 750°C in comparison to $0.33 \text{ W}\cdot\text{cm}^{-2}$ for the Zn-free composite.

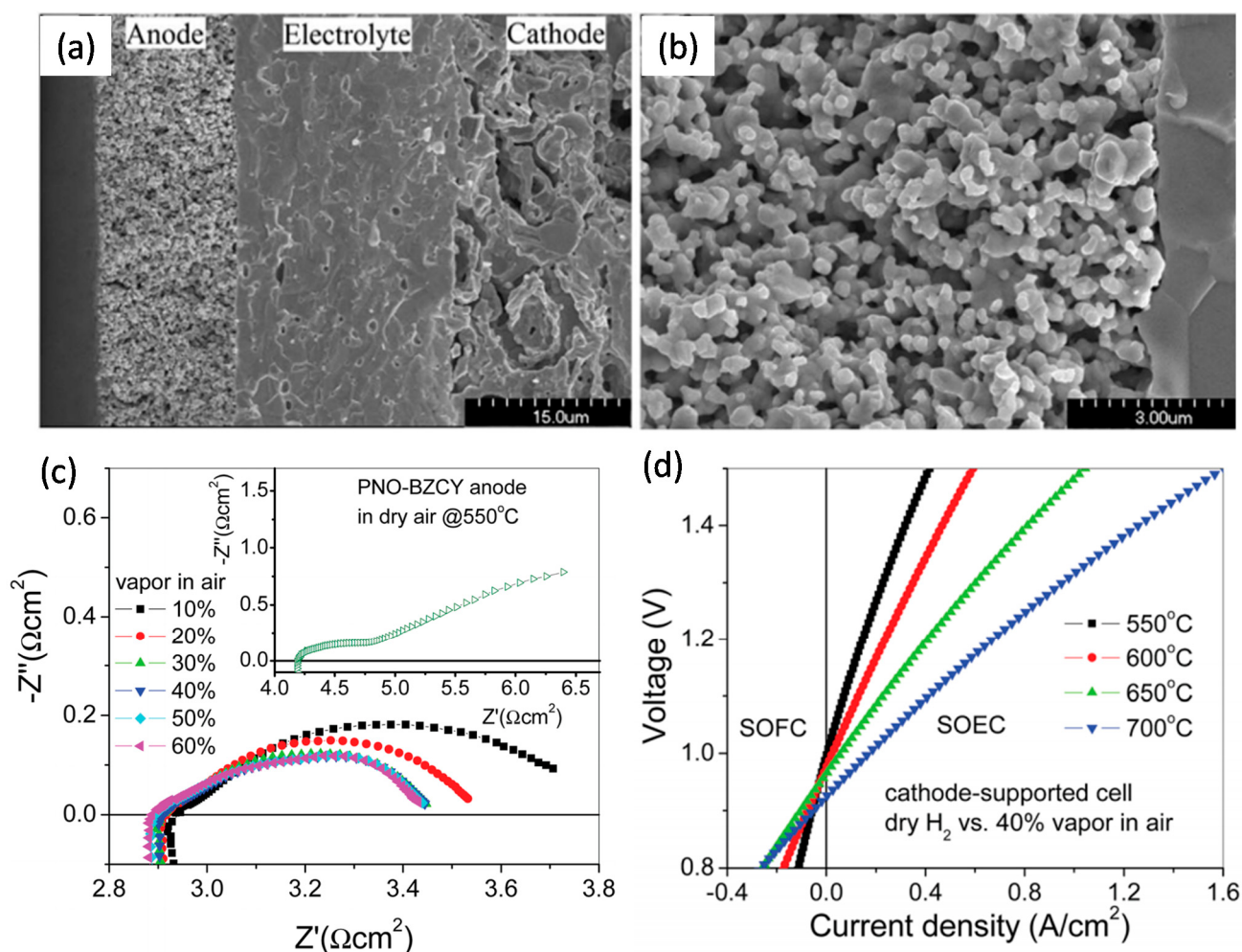


Figure 8. SEM image of a protonic ceramic electrolysis cell based on a Pr_2NiO_4 -BCZY62 composite as anode, BCZY62 as electrolyte, and Ni-BCZY62 as cathode (a); magnified anode component and corresponding anode–electrolyte interface (b); impedance spectra of the half cell in three-electrode configuration with Pr_2NiO_4 -BCZY62 composite anode in air at 550°C with different humidifications (c); current–voltage curves of the single cell in electrolysis mode, with dry H_2 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 $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$, prepared with 10 at % Ba deficiency to improve chemical stability in CO_2 - and H_2O -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 $0.537 \text{ W}\cdot\text{cm}^{-2}$ was

achieved with the composite at 700 °C. A cobalt-free, triple-conducting simple perovskite $\text{Ba}_{0.95}\text{La}_{0.05}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{3-\delta}$, used in a composite with BCZYb7111, reached a single-cell power density of $0.329 \text{ W}\cdot\text{cm}^{-2}$ 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 $1.02 \text{ W}\cdot\text{cm}^{-2}$ at 700 °C and a very low R_p of $0.051 \Omega\cdot\text{cm}^2$, 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.

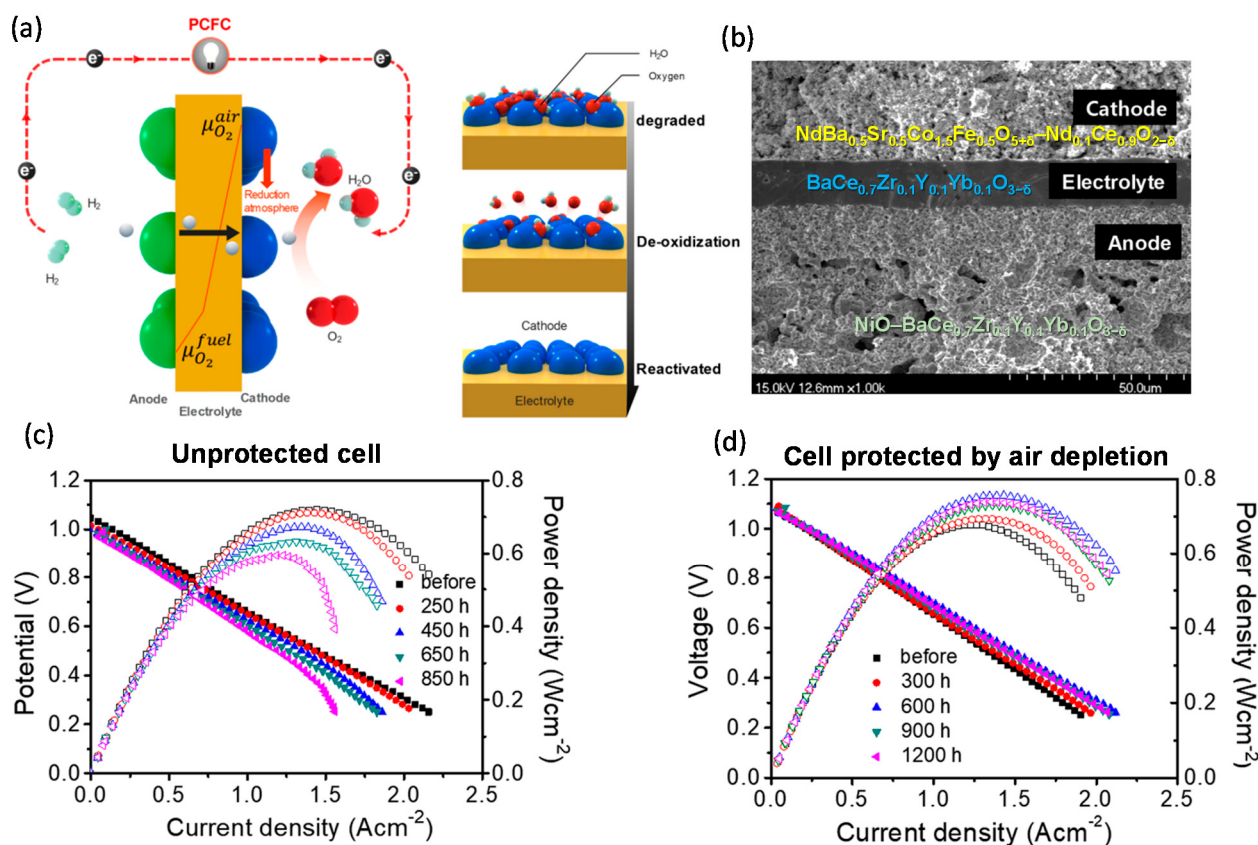


Figure 9. Schematic diagram of electrochemical potential levels during single-cell operation and operational protocol to prevent cathode surface degradation (a); scanning electron micrograph of a protonic ceramic single cell based on a $\text{NdBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_{5+\delta}$ – $\text{Nd}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ composite cathode over a BCZYb7111 electrolyte and NiO –BCZYb7111 anode (b); performance of the PCFC before and after operation for different periods of time under a galvanostatic condition of $0.5 \text{ A}\cdot\text{cm}^{-2}$ 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 ($\Omega \cdot \text{cm}^2$)	MPD ($\text{W} \cdot \text{cm}^{-2}$)	Electrolyte	Thickness (μm)	Ref
Mixed proton–electron-conducting cathodes					
$\text{BaCe}_{0.1}\text{Zr}_{0.2}\text{Y}_{0.1}\text{Fe}_{0.6}\text{O}_{3-\delta}$	0.21 (700 °C)	0.240 (700 °C)	BCZYYb7111	30	[33]
$\text{BaCe}_{0.9-y}\text{Pr}_y\text{Gd}_{0.1}\text{O}_{3-\delta}$	0.47 (800 °C)	-	BCG20	510	[21]
$\text{BaPr}_{0.8}\text{In}_{0.2}\text{O}_{3-\delta}$	0.09 (700 °C)	0.550 (700 °C)	BCZYYb7111	15	[25]
$\text{BaZr}_{0.2}\text{Fe}_{0.6}\text{Y}_{0.2}\text{O}_{3-\delta}$	0.28 (700 °C)	0.322 (700 °C)	BCZY71	20	[32]
$\text{BaZr}_{0.6}\text{Co}_{0.4}\text{O}_{3-\delta}$	0.19 (700 °C)	-	BCZY53	20	[31]
Mixed oxide-ion–electron-conducting cathodes					
$\text{Ba}_{0.5}\text{La}_{0.5}\text{CoO}_3$	1.4 (600 °C)	-	$\text{Ba}(\text{Zr}_{0.5}\text{Ce}_{0.4})_{8/9}\text{Y}_{0.2}\text{O}_{3-\delta}$	12	[45]
$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{3-\delta}$	0.08 (700 °C)	0.486 (700 °C)	BCZY71	15	[62]
$\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Ce}_{0.1}\text{Gd}_{0.1}\text{O}_{3-\delta}$	0.12 (650 °C)	0.663 (700 °C)	BCZYYb7111	30	[57]
$\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Ce}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$	0.13 (650 °C)	0.648 (700 °C)	BCZYYb7111	30	[57]
$\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.2}\text{O}_{3-\delta}$	1 (600 °C)	0.225 (600 °C)	BCZYYb7111	60	[56]
BSCF	0.06 (700 °C)	0.800 (700 °C)	$\text{BaZr}_{0.4}\text{Ce}_{0.45}\text{Y}_{0.15}\text{O}_{3-\delta}$	15.5	[53]
$\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$	0.17 (700 °C)	0.290 (700 °C)	BCZY53	20	[69]
$\text{Ca}_{3-x}\text{La}_x\text{Co}_4\text{O}_{9+\delta}$ (x = 0, 0.3)	2.2 (600 °C)	-	BCY10	-	[68]
$\text{La}_{0.6}\text{Ba}_{0.4}\text{CoO}_{3-\delta}$	-	0.180 (1000 °C)	BCS10	500	[39]
LSC55	0.38 (700 °C)	0.300 (700 °C)	BCZY71	500	[40]
LSCF	-	0.079 (700 °C)	BCZY27	20	[47]
LSCF	-	0.018 (600 °C)	BCZY62	500	[48]
LSCF	1.12 (700 °C)	0.268 (700 °C)	BCZYYb7111	60	[49]
LSCF: BaCO_3	0.29 (700 °C)	0.404 (700 °C)	BCZYYb7111	60	[49]
LSCF	0.26 (700 °C)	0.753 (700 °C)	$\text{BaCe}_{0.95}\text{Tb}_{0.05}\text{O}_{3-\delta}$	12–15	[46]
$\text{Nd}_{0.5}\text{Ba}_{0.5}\text{Fe}_{0.9}\text{Co}_{0.1}\text{O}_{3-\delta}$	0.18 (700 °C)	0.390 (700 °C)	BCZY53	30	[63]
$\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$	0.09 (700 °C)	0.348 (700 °C)	BCZY44	20	[44]
$\text{SrCo}_{0.9}\text{Sb}_{0.1}\text{O}_{3-\delta}$	0.14 (700 °C)	0.259 (700 °C)	BCZY71	20	[42]
$\text{SrFe}_{0.95}\text{Nb}_{0.05}\text{O}_{3-\delta}$	0.23 (650 °C)	0.538 (650 °C)	BCZY71	20	[61]
SSC	10 (700 °C)	$5.9 \cdot 10^{-3}$ (700 °C)	BCZY62	500	[43]
$\text{Y}_{0.8}\text{Ca}_{0.2}\text{BaCo}_4\text{O}_7$	0.12 (700 °C)	0.472 (700 °C)	BCZY71	20	[65]
$\text{Y}_{0.8}\text{Ca}_{0.2}\text{BaCo}_4\text{O}_7$	-	0.308 (725 °C)	BCZY53	30	[66]
Triple protonic oxide ionic electron hole-conducting oxides					
$\text{Ba}(\text{Co}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1})_{0.95}\text{O}_{3-\delta}$	0.80 (550 °C)	0.840 (650 °C)	$\text{Ba}(\text{Zr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1})_{0.95}\text{O}_{3-\delta}$	12	[119]
$\text{Ba}(\text{Zr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1})_{0.95}\text{O}_{3-\delta}$	0.61 (550 °C)	0.450 (550 °C)	BCZYYb7111	25	[121]
$\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Co}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$	0.36 (700 °C)	0.580 (700 °C)	BCZYYb4411	22	[120]
$\text{Ba}_{0.9}\text{Co}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$	0.52 (500 °C)	0.797 (650 °C)	BCZY71	40	[118]
$\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$	-	0.455 (500 °C)	BCZYYb7111	20–30	[115]
$\text{BaFe}_{0.5}\text{Sn}_{0.2}\text{Bi}_{0.3}\text{O}_{3-\delta}$	0.03 (700 °C)	1.280 (700 °C)	BCZY71	12	[125]
$\text{BaGd}_{0.8}\text{La}_{0.2}\text{Co}_2\text{O}_{6-\delta}$	0.05 (650 °C)	-	BCZY71	-	[100]
BSCF	0.18 (650 °C)	0.622 (650 °C)	BCZYYb7111	21.3	[106]
GBCO	0.16 (700 °C)	0.266 (700 °C)	BCZY71	10	[94]
GdBaCuCoO_{5+x}	0.17 (700 °C)	0.480 (700 °C)	BCZY71	20	[107]
$\text{La}_{1.2}\text{Sr}_{0.8}\text{Ni}_{0.6}\text{Fe}_{0.4}\text{O}_{4-\delta}$	0.08 (700 °C)	0.781 (700 °C)	BCZY71	15	[86]

Table 3. Cont.

Air Electrode	ASR ($\Omega \cdot \text{cm}^2$)	MPD ($\text{W} \cdot \text{cm}^{-2}$)	Electrolyte	Thickness (μm)	Ref
$\text{La}_{1.5}\text{Ca}_{0.5}\text{NiO}_{4-\delta}$	0.05 (700 °C)	0.923 (700 °C)	BCZY71	15	[87]
$\text{La}_3\text{Ni}_{1.6}\text{Fe}_{0.4}\text{O}_7$	0.15 (700 °C)	0.398 (700 °C)	BCZY53	20	[88]
LaBaCuCoO_{5-x}	0.15 (700 °C)	0.432 (700 °C)	BCZY71	20	[97]
LaBaCuFeO_{5+x}	0.27 (700 °C)	0.327 (700 °C)	BCZY71	20	[97]
$\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$	0.13 (700 °C)	0.550 (700 °C)	BCZY71	15	[90]
$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$	3.48 (650 °C)	0.410 (650 °C)	BCZY71	24	[92]
NBSCF	0.08 (700 °C)	1.370 (700 °C)	BCZYYb7111	14.7	[98]
$\text{Nd}_2\text{NiO}_{4-\delta}$	4.8 (600 °C)	0.060 (600 °C)	BCY10	25	[79]
PBSCF	0.13 (600 °C)	0.500 (500 °C)	BCZYYb4411	15	[101]
PBSCF	0.30 (600 °C)	0.650 (600 °C)	BCZYYb6211	7.6	[103]
PBSCF	-	1.100 (650 °C)	BCZYYb4411	15	[102]
$\text{Pr}_2\text{BaNiMnO}_{7-\delta}$	0.084 (700 °C)	1.070 (700 °C)	BCZYYb7111	20	[108]
$\text{Pr}_2\text{NiO}_{4-\delta}$	0.70 (650 °C)	0.130 (650 °C)	BCY10	85	[77]
$\text{Pr}_2\text{NiO}_{4-\delta}$	0.06 (650 °C)	0.820 (650 °C)	$\text{BaCe}_{0.55}\text{Zr}_{0.3}\text{Y}_{0.15}\text{O}_{3-\delta}$	5	[82]
$(\text{PrBa}_{0.8}\text{Ca}_{0.2})_{0.95}\text{Co}_2\text{O}_{6-\delta}$	0.14 (600 °C)	0.540 (600 °C)	BCZYYb6211	20	[105]
$\text{PrNi}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$	0.05 (500 °C)	0.611 (600 °C)	BCZYYb4411	10	[114]
$\text{SmBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+\delta}$	0.08 (700 °C)	0.533 (700 °C)	BCZY71	15	[97]
$\text{SmBaCo}_2\text{O}_{5+x}$	0.15 (700 °C)	0.382 (700 °C)	BCZY71	25	[95]
$\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.4}\text{Zr}_{0.1}\text{O}_{6-\delta}$	0.17 (700 °C)	0.790 (700 °C)	BCZYYb7111	20	[159]
$\text{Sr}_2\text{Sc}_{0.1}\text{Nb}_{0.1}\text{Co}_{1.5}\text{Fe}_{0.3}\text{O}_{6-\delta}$	0.14 (650 °C)	0.840 (650 °C)	BCZYYb7111	18.5	[106]
Composite cathodes					
$\text{Ba}_{0.4}\text{K}_{0.1}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$: BCZY71	0.05 (700 °C)	1.275 (750 °C)	BCZY71	10	[152]
$\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Fe}_{0.85}\text{Sn}_{0.05}\text{Y}_{0.1}\text{O}_{3-\delta}$: SDC	0.05 (700 °C)	0.950 (700 °C)	BCZY71	17	[171]
$\text{Ba}_{0.95}\text{La}_{0.05}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{3-\delta}$: BCZY71	0.08 (750 °C)	0.330 (750 °C)	BCZYYb7111	42	[197]
$\text{Ba}_{0.9}\text{Co}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$: BCZY71	0.15 (700 °C)	0.540 (700 °C)	BCZY71	25	[196]
$\text{Ba}_4\text{Sr}_2\text{Sm}_2\text{Co}_4\text{O}_{15}$: $\text{BaCe}_{0.5}\text{Pr}_{0.3}\text{Y}_{0.2}\text{O}_{3-\delta}$	0.20 (600 °C)	0.197 (600 °C)	BCY10	60	[139]
$\text{BaCe}_{0.4}\text{Fe}_{0.4}\text{Co}_{0.2}\text{O}_{3-\delta}$	0.075 (700 °C)	0.335 (700 °C)	BCZYYb7111	70	[169]
$\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$: BCZYYb7111	0.25 (600 °C)	0.660 (600 °C)	BCZYYb7111	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: BCZYYb7111	0.27 (600 °C)	0.420 (600 °C)	BCZYYb7111	4	[150]
$\text{Ca}_{0.3}\text{Y}_{0.7}\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$: BCZY71	0.07 (750 °C)	0.798 (750 °C)	BCZY71	150	[146]
$\text{La}_{0.35}\text{Pr}_{0.15}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$: Pr	0.06 (700 °C)	1.080 (700 °C)	BCZY71	18	[166]
$\text{La}_{0.8}\text{Ba}_{0.2}\text{CoO}_{3-\delta}$: $\text{BaZr}_{0.6}\text{Co}_{0.4}\text{O}_{3-\delta}$	1.54 (600 °C)	-	BZY10	-	[140]
$\text{La}_{0.6}\text{Ba}_{0.4}\text{CoO}_{3-\delta}$: $\text{BaZr}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$	1.76 (600 °C)	-	BZY10	-	[140]
$\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_{4-\delta}$: LSM55	0.08 (700 °C)	0.940 (700 °C)	BCZY71	12	[179]
$\text{La}_{0.62}\text{Ba}_{0.38}\text{CoO}_{3-\delta}$: $\text{BaZr}_{0.68}\text{Y}_{0.07}\text{Co}_{0.25}\text{O}_{3-\delta}$	0.21 (600 °C)	-	BZY10	-	[141]
$\text{La}_{0.6}\text{Ba}_{0.4}\text{CoO}_{3-\delta}$: BCZYYb7111	0.02 (700 °C)	1.000 (700 °C)	BCZYYb7111	10	[147]
$\text{La}_2\text{NiO}_{4+\delta}$: $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$	0.09 (700 °C)	0.590 (700 °C)	BCZY71	20	[164]
$\text{La}_2\text{NiO}_{4+\delta}$: BCZY71	6.7 (700 °C)	0.032 (700 °C)	BCZY71	25	[183]
$\text{La}_2\text{NiO}_{4+\delta}$: $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$	0.03 (700 °C)	0.969 (700 °C)	BCZY71	-	[187]

Table 3. Cont.

Air Electrode	ASR ($\Omega \cdot \text{cm}^2$)	MPD ($\text{W} \cdot \text{cm}^{-2}$)	Electrolyte	Thickness (μm)	Ref
LaCoO ₃ : BCZY27	0.11 (600 °C)	-	BCZY27	-	[138]
LSCF: BaCe _{0.5} Zr _{0.35} Y _{0.15} O _{3-δ}	0.18 (700 °C)	0.537 (700 °C)	BaCe _{0.5} Zr _{0.35} Y _{0.15} O _{3-δ}	8	[145]
LSCF: BCYb10	0.14 (700 °C)	0.050 (700 °C)	BCY20	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(Ce _{0.51} Zr _{0.30} Y _{0.15} Zn _{0.04})O _{3-δ}	0.09 (700 °C)	0.425 (700 °C)	Ba(Ce _{0.51} Zr _{0.30} Y _{0.15} Zn _{0.04})O _{3-δ}	70	[156]
LSM82: La _{0.995} Ca _{0.005} NbO ₄	25 (750 °C)	-	La _{0.995} Ca _{0.005} NbO ₄	-	[174]
LSM82: La _{5.5} WO _{12-δ}	8 (750 °C)	-	La _{5.5} WO _{12-δ}	-	[175]
LSM82: BCY15	0.11 (750 °C)	0.394 (750 °C)	BCY15	15	[178]
LSM82: La _{5.5} WO _{11.25-δ} : 20SDC	1.4 (750 °C)	-	La _{5.5} WO _{11.25-δ}	-	[176]
LSM82: La _{28-x} W _{4+x} O _{54+3x/2}	40 (650 °C)	-	La _{28-x} W _{4+x} O _{54+3x/2}	-	[177]
LSM82: 50LDC	0.69 (800 °C)	0.065 (800 °C)	La _{0.99} Ca _{0.01} NbO ₄	20	[173]
LSM82: BCZY71: Pr	0.33 (700 °C)	-	BCZY71	-	[180]
Nd(Ba _{0.75} Ca _{0.25}) Co _{1.5} Fe _{0.4} Ni _{0.1} O _{5+δ} : 10GDC	0.091 (650 °C)	0.880 (650 °C)	BCZYYb7111	20	[191]
Nd _{0.5} Ba _{0.5} Fe _{0.9} Ni _{0.1} O _{3-δ} : BCZY71	0.15 (700 °C)	0.490 (700 °C)	BCZY71	40	[151]
Nd _{0.5} Ba _{0.5} Fe _{0.9} Ni _{0.1} O _{3-δ} : BCZY71	0.15 (700 °C)	0.490 (700 °C)	BCZY71	40	[168]
Nd _{1.95} NiO _{4-δ} : BCZYYb7111	0.43 (750 °C)	0.154 (750 °C)	BCZYYb7111	60	[182]
NdBa _{0.5} Sr _{0.5} Co _{1.5} Fe _{0.5} O _{5-δ} : Ce _{0.9} Nd _{0.1} O _{2-δ}	0.18 (650 °C)	0.719 (650 °C)	BCZYYb7111	20	[190]
PBCO: BCZY71: 10GDC	0.05 (700 °C)	1.020 (700 °C)	BCZY71	12	[199]
PBCO: BCZYYb7111	0.08 (750 °C)	0.490 (750 °C)	BCZYYb7111	30	[193]
Pr _{0.58} Sr _{0.4} Fe _{0.8} Co _{0.2} O _{3-δ} : BCYb10	0.50 (700 °C)	-	BCYb10	20	[167]
Pr _{0.6} Sr _{0.4} Cu _{0.2} Fe _{0.8} O _{3-δ} : 20SDC	0.14 (650 °C)	0.456 (650 °C)	BCZY53	20	[165]
Pr _{0.6} Sr _{0.4} Cu _{0.2} Fe _{0.8} O _{3-δ} : 20SDC	-	0.556 (650 °C)	BCZY71	14	[165]
(Pr _{0.9} La _{0.1}) ₂ (Ni _{0.74} Cu _{0.21} Nb _{0.05}) O _{4+δ} : BCZY71	0.13 (700 °C)	0.770 (700 °C)	BCZY71	12	[184]
Pr _{1.7} Ca _{0.3} NiO _{4+δ} : BaCe _{0.8} Gd _{0.19} Cu _{0.01} O _{3-δ}	0.26 (700 °C)	0.170 (700 °C)	BaCe _{0.8} Gd _{0.19} Cu _{0.01} O _{3-δ}	25	[188]
Pr _{1.9} Ba _{0.1} NiO _{4-δ} : BaCe _{0.5} Zr _{0.3} Dy _{0.2} O _{3-δ}	0.43 (700 °C)	0.470 (700 °C)	BaCe _{0.5} Zr _{0.3} Dy _{0.2} O _{3-δ}	30	[185]
Pr ₂ NiO ₄ : BCZY62	0.31 (700 °C)	0.977 (700 °C)	BCZY62	20	[186]
PrBa _{0.9} Ca _{0.1} Co _{1.85} Zn _{0.15} O _{5+δ} : BCZYYb7111	0.04 (750 °C)	0.870 (750 °C)	BCZYYb7111	17	[195]
PrBaCo _{1.75} Ta _{0.25} O _{5+δ} : BCZYYb7111	0.05 (700 °C)	0.755 (700 °C)	BCZYYb7111	10	[194]
Sr ₂ Fe _{1.5} Mo _{0.5} O _{6-δ} : BZY20	0.48 (600 °C)	-	BZY20	16	[160]
(SrBa) _{0.6} Pr _{0.4} (CuTi) _{0.2} Fe _{0.8} O _{3-δ} : 20SDC	0.07 (750 °C)	0.925 (750 °C)	BCZY71	13	[172]
SrCo _{0.7} Fe _{0.2} Zr _{0.1} O _{3-δ} : BCZY71	-	0.129 (700 °C)	BCZY71	-	[142]
SrCo _{0.8} Fe _{0.15} Zr _{0.05} O _{3-δ} : BCZYYb7111	0.07 (700 °C)	0.712 (700 °C)	BCZYYb7111	38	[132]
SrEu ₂ Fe _{1.8} Co _{0.2} O _{7-δ} : BCZY71	0.13 (700 °C)	0.560 (700 °C)	BCZY71	15	[189]
SSC: BaCe _{0.5} Zr _{0.35} Y _{0.15} O _{3-δ}	0.18 (700 °C)	0.642 (700 °C)	BaCe _{0.5} Zr _{0.35} Y _{0.15} O _{3-δ}	10	[131]
SSC: BaCe _{0.5} Zr _{0.3} Y _{0.16} Zn _{0.04} O _{3-δ}	0.15 (700 °C)	0.528 (700 °C)	BaCe _{0.5} Zr _{0.3} Y _{0.16} Zn _{0.04} O _{3-δ}	20	[128]

Table 3. Cont.

Air Electrode	ASR ($\Omega \cdot \text{cm}^2$)	MPD ($\text{W} \cdot \text{cm}^{-2}$)	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: $\text{SmBaCo}_2\text{O}_{5+\delta}$	0.02 (750 °C)	1.570 (750 °C)	BCZYYb7111	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 $\text{Ba}(\text{Ce},\text{Y})\text{O}_{3-\delta}$, $\text{Ba}(\text{Zr},\text{Y})\text{O}_{3-\delta}$, 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 monophasic 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 $\text{Pr}_2\text{NiO}_{4+\delta}$ and $\text{PrBaCo}_2\text{O}_{5+\delta}$, 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.

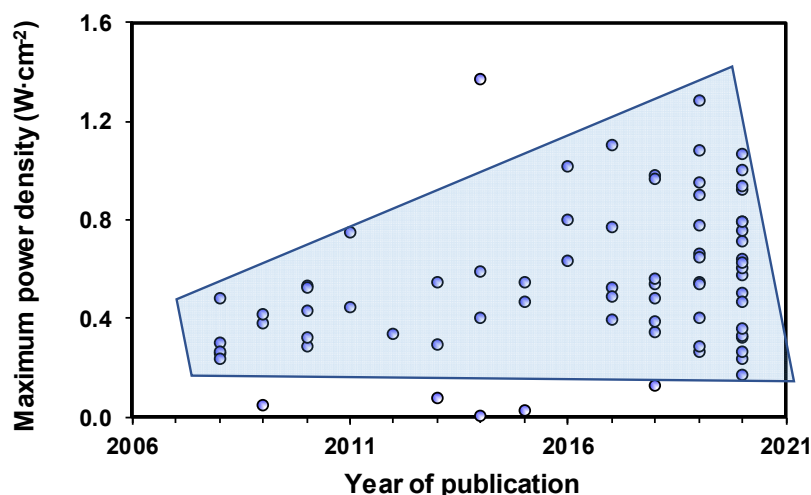


Figure 10. Evolution of reported maximum power densities at 700 °C for protonic ceramic fuel cells.

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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References

1. Winter, C.-J. Hydrogen energy—Abundant, efficient, clean: A debate over the energy-system-of-change. *Int. J. Hydrog. Energy* **2009**, *34*, S1–S52. [\[CrossRef\]](#)
2. Minh, N.Q. Ceramic Fuel Cells. *J. Am. Ceram. Soc.* **1993**, *76*, 563–588. [\[CrossRef\]](#)
3. Ormerod, R.M. Solid oxide fuel cells. *Chem. Soc. Rev.* **2003**, *32*, 17–28. [\[CrossRef\]](#) [\[PubMed\]](#)
4. Brett, D.J.L.; Atkinson, A.; Brandon, N.P.; Skinner, S.J. Intermediate temperature solid oxide fuel cells. *Chem. Soc. Rev.* **2008**, *37*, 1568–1578. [\[CrossRef\]](#)
5. Coors, W.G. Protonic ceramic fuel cells for high-efficiency operation with methane. *J. Power Sources* **2003**, *118*, 150–156. [\[CrossRef\]](#)
6. Iwahara, H.; Esaka, T.; Uchida, H.; Maeda, N. Proton conduction in sintered oxides and its application to steam electrolysis for hydrogen production. *Solid State Ion.* **1981**, *3–4*, 359–363. [\[CrossRef\]](#)
7. Iwahara, H. Technological challenges in the application of proton conducting ceramics. *Solid State Ion.* **1995**, *77*, 289–298. [\[CrossRef\]](#)

8. Duan, C.; Huang, J.; Sullivan, N.; O'Hayre, R. Proton-conducting oxides for energy conversion and storage. *Appl. Phys. Rev.* **2020**, *7*, 011314. [\[CrossRef\]](#)
9. Duan, C.; Kee, R.; Zhu, H.; Sullivan, N.; Zhu, L.; Bian, L.; Jennings, D.; O'Hayre, R. Highly efficient reversible protonic ceramic electrochemical cells for power generation and fuel production. *Nat. Energy* **2019**, *4*, 230–240. [\[CrossRef\]](#)
10. Medvedev, D. Trends in research and development of protonic ceramic electrolysis cells. *Int. J. Hydrog. Energy* **2019**, *44*, 26711–26740. [\[CrossRef\]](#)
11. Lei, L.; Zhang, J.; Yuan, Z.; Liu, J.; Ni, M.; Chen, F. Progress Report on Proton Conducting Solid Oxide Electrolysis Cells. *Adv. Funct. Mater.* **2019**, *29*. [\[CrossRef\]](#)
12. Ni, M.; Leung, M.K.H.; Leung, D.Y.C. Theoretical analysis of reversible solid oxide fuel cell based on proton-conducting electrolyte. *J. Power Sources* **2008**, *177*, 369–375. [\[CrossRef\]](#)
13. Tsai, C.-L.; Schmidt, V.H. Fabrication, Performance, and Model for Proton Conductive Solid Oxide Fuel Cell. *J. Electrochem. Soc.* **2011**, *158*, B885. [\[CrossRef\]](#)
14. Asano, K.; Hibino, T.; Iwahara, H. A Novel Solid Oxide Fuel Cell System Using the Partial Oxidation of Methane. *J. Electrochem. Soc.* **1995**, *142*, 3241–3245. [\[CrossRef\]](#)
15. Luisetto, I.; Di Bartolomeo, E.; D'Epifanio, A.; Licoccia, S. CO₂/CH₄ Reforming High Temperature Proton Conductor (HTPC) Fuel Cells. *J. Electrochem. Soc.* **2011**, *158*, B1368. [\[CrossRef\]](#)
16. Uchida, H.; Tanaka, S.; Iwahara, H. Polarization at Pt electrodes of a fuel cell with a high temperature-type proton conductive solid electrolyte. *J. Appl. Electrochem. Soc.* **1985**, *15*, 93–97. [\[CrossRef\]](#)
17. Fleig, J. Solid Oxide Fuel Cell Cathodes: Polarization Mechanisms and Modeling of the Electrochemical Performance. *Annu. Rev. Mater. Res.* **2003**, *33*, 361–382. [\[CrossRef\]](#)
18. Zhu, H.; Kee, R.J. Modeling Protonic-Ceramic Fuel Cells with Porous Composite Electrodes in a Button-Cell Configuration. *J. Electrochem. Soc.* **2017**, *164*, F1400–F1411. [\[CrossRef\]](#)
19. Fabbri, E.; Pergolesi, D.; Traversa, E. Electrode materials: A challenge for the exploitation of protonic solid oxide fuel cells. *Sci. Technol. Adv. Mater.* **2010**, *11*. [\[CrossRef\]](#)
20. Mukundan, R.; Davies, P.K.; Worrell, W.L. Electrochemical Characterization of Mixed Conducting Ba(Ce_{1-(x+y)}Pr_yGd_x)O_{3-x/2} Cathodes. *MRS Online Proc. Libr.* **1996**, *453*, 573. [\[CrossRef\]](#)
21. Mukundan, R.; Davies, P.; Worrell, W. Electrochemical Characterization of Mixed Conducting Ba(Ce_{0.8-y}Pr_yGd_{0.2})O_{2.9} Cathodes. *J. Electrochem. Soc.* **2001**, *148*, 82–86. [\[CrossRef\]](#)
22. Furoy, K.A.; Haugsrud, R.; Hänsel, M.; Magrasó, A.; Norby, T. Role of protons in the electrical conductivity of acceptor-doped BaPrO₃, BaTbO₃ and BaThO₃. *Solid State Ion.* **2007**, *178*, 461–467. [\[CrossRef\]](#)
23. Magrasó, A.; Espiell, F.; Segarra, M.; Irvine, J.T.S. Chemical and electrical properties of BaPr_{0.7}Gd_{0.3}O_{3-δ}. *J. Power Sources* **2007**, *169*, 53–58. [\[CrossRef\]](#)
24. Magrasó, A.; Haugsrud, R.; Segarra, M.; Norby, T. Defects and transport in Gd-doped BaPrO₃. *J. Electroceramics* **2009**, *23*, 80–88. [\[CrossRef\]](#)
25. Wang, Z.; Liu, M.; Sun, W.; Ding, D.; Lü, Z.; Liu, M. A mixed-conducting BaPr_{0.8}In_{0.2}O_{3-δ} cathode for proton-conducting solid oxide fuel cells. *Electrochem. Commun.* **2013**, *27*, 19–21. [\[CrossRef\]](#)
26. Fabbri, E.; Markus, I.; Bi, L.; Pergolesi, D.; Traversa, E. Tailoring mixed proton-electronic conductivity of BaZrO₃ by Y and Pr co-doping for cathode application in protonic SOFCs. *Solid State Ion.* **2011**, *202*, 30–35. [\[CrossRef\]](#)
27. Magrasó, A.; Frontera, C.; Gunnæs, A.E.; Tarancón, A.; Marrero-López, D.; Norby, T.; Haugsrud, R. Structure, chemical stability and mixed proton-electron conductivity in BaZr_{0.9-x}Pr_xGd_{0.1}O_{3-δ}. *J. Power Sources* **2011**, *196*, 9141–9147. [\[CrossRef\]](#)
28. Heras-Juaristi, G.; Amador, U.; Romero de Paz, J.; Fuentes, R.O.; Chinelatto, A.L.; Ritter, C.; Fagg, D.P.; Pérez-Coll, D.; Mather, G.C. Structures, Phase Fields, and Mixed Protonic–Electronic Conductivity of Ba-Deficient, Pr-Substituted BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{3-δ}. *Inorg. Chem.* **2018**, *57*, 15023–15033. [\[CrossRef\]](#)
29. Heras-Juaristi, G.; Amador, U.; Fuentes, R.O.; Chinelatto, A.L.; Romero De Paz, J.; Ritter, C.; Fagg, D.P.; Pérez-Coll, D.; Mather, G.C. Thermal evolution of structures and conductivity of Pr-substituted BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{3-δ}: Potential cathode components for protonic ceramic fuel cells. *J. Mater. Chem. A* **2018**, *6*, 5324–5334. [\[CrossRef\]](#)
30. Kim, D.Y.; Miyoshi, S.; Tsuchiya, T.; Yamaguchi, S. Defect Chemistry and Electrochemical Properties of BaZrO₃ Heavily Doped with Fe. *Ecs Trans.* **2012**, *45*, 161–170. [\[CrossRef\]](#)
31. Rao, Y.; Zhong, S.; He, F.; Wang, Z.; Peng, R.; Lu, Y. Cobalt-doped BaZrO₃: A single phase air electrode material for reversible solid oxide cells. *Int. J. Hydrog. Energy* **2012**, *37*, 12522–12527. [\[CrossRef\]](#)
32. Wu, Y.; Li, K.; Yang, Y.; Song, W.; Ma, Z.; Chen, H.; Ou, X.; Zhao, L.; Khan, M.; Ling, Y. Investigation of Fe-substituted in BaZr_{0.8}Y_{0.2}O_{3-δ} proton conducting oxides as cathode materials for protonic ceramics fuel cells. *J. Alloy. Compd.* **2020**, *814*. [\[CrossRef\]](#)
33. Tarutina, L.R.; Vdovin, G.K.; Lyagaeva, J.G.; Medvedev, D.A. BaCe_{0.7-x}Zr_{0.2}Y_{0.1}Fe_xO_{3-δ} derived from proton-conducting electrolytes: A way of designing chemically compatible cathodes for solid oxide fuel cells. *J. Alloy. Compd.* **2020**, *831*. [\[CrossRef\]](#)
34. Hui, Z.; Michèle, P. Preparation, chemical stability, and electrical properties of Ba(Ce_{1-x}Bi_x)O₃ (x = 0.0–0.5). *J. Mater. Chem.* **2002**, *12*, 3787–3791. [\[CrossRef\]](#)

35. Magrasó, A.; Fontaine, M.L.; Larring, Y.; Bredesen, R.; Syvertsen, G.E.; Lein, H.L.; Grande, T.; Huse, M.; Strandbakke, R.; Haugrud, R.; et al. Development of proton conducting SOFCs based on LaNbO_4 electrolyte—Status in Norway. *Fuel Cells* **2011**, *11*, 17–25. [\[CrossRef\]](#)
36. Solís, C.; Serra, J.M. Adjusting the conduction properties of $\text{La}_{0.995}\text{Ca}_{0.005}\text{NbO}_{4-\delta}$ by doping for proton conducting fuel cells electrode operation. *Solid State Ion.* **2011**, *190*, 38–45. [\[CrossRef\]](#)
37. Badwal, S.P.S. Stability of solid oxide fuel cell components. *Solid State Ion.* **2001**, *143*, 39–46. [\[CrossRef\]](#)
38. Wang, N.; Hinokuma, S.; Ina, T.; Toriumi, H.; Katayama, M.; Inada, Y.; Zhu, C.; Habazaki, H.; Aoki, Y. Incorporation of bulk proton carriers in cubic perovskite manganite driven by interplays of oxygen and manganese redox. *Chem. Mater.* **2019**, *31*, 8383–8393. [\[CrossRef\]](#)
39. Iwahara, H.; Yajima, T.; Hibino, T.; Ushida, H. Performance of Solid Oxide Fuel Cell Using Proton and Oxide Ion Mixed Conductors Based on $\text{BaCe}_{1-x}\text{Sm}_x\text{O}_{3-\delta}$. *J. Electrochem. Soc.* **1993**, *140*, 1687–1691. [\[CrossRef\]](#)
40. Xie, K.; Yan, R.; Dong, D.; Wang, S.; Chen, X.; Jiang, T.; Lin, B.; Wei, M.; Liu, X.; Meng, G. A modified suspension spray combined with particle gradation method for preparation of protonic ceramic membrane fuel cells. *J. Power Sources* **2008**, *179*, 576–583. [\[CrossRef\]](#)
41. Aguadero, A.; Alonso, J.A.; Escudero, M.J.; Daza, L. Structural and Electrical Characterization of the Novel $\text{SrCo}_{0.9}\text{Sb}_{0.1}\text{O}_{3-\delta}$ Perovskite: Evaluation as a Solid Oxide Fuel Cell Cathode Material. *Chem. Mater.* **2007**, *19*, 6437–6444. [\[CrossRef\]](#)
42. Ding, H.; Lin, B.; Jiang, Y.; Wang, S.; Fang, D.; Dong, Y.; Tao, S.; Peng, R.; Liu, X.; Meng, G. Low-temperature protonic ceramic membrane fuel cells (PCMFCs) with $\text{SrCo}_{0.9}\text{Sb}_{0.1}\text{O}_{3-\delta}$ cubic perovskite cathode. *J. Power Sources* **2008**, *185*, 937–940. [\[CrossRef\]](#)
43. Oda, H.; Yoneda, T.; Sakai, T.; Okuyama, Y.; Matsumoto, H. Preparation of nano-structured cathode for protonic ceramic fuel cell by bead-milling method. *Solid State Ion.* **2014**, *262*, 388–391. [\[CrossRef\]](#)
44. Wang, B.; Bi, L.; Zhao, X.S. Liquid-phase synthesis of $\text{SrCo}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ cathode material for proton-conducting solid oxide fuel cells. *Ceram. Int.* **2018**, *44*, 5139–5144. [\[CrossRef\]](#)
45. Leonard, K.; Okuyama, Y.; Takamura, Y.; Lee, Y.S.; Miyazaki, K.; Ivanova, M.E.; Meulenberg, W.A.; Matsumoto, H. Efficient intermediate-temperature steam electrolysis with Y:SrZrO_3 – SrCeO_3 and Y:BaZrO_3 – BaCeO_3 proton conducting perovskites. *J. Mater. Chem. A* **2018**, *6*, 19113–19124. [\[CrossRef\]](#)
46. Meng, X.; Yang, N.; Song, J.; Tan, X.; Ma, Z.F.; Li, K. Synthesis and characterization of terbium doped barium cerates as a proton conducting SOFC electrolyte. *Int. J. Hydrog. Energy* **2011**, *36*, 13067–13072. [\[CrossRef\]](#)
47. Robinson, S.; Manerbino, A.; Grover Coors, W.; Sullivan, N.P. Fabrication and Performance of Tubular, Electrode-Supported $\text{BaCe}_{0.2}\text{Zr}_{0.7}\text{Y}_{0.1}\text{O}_{3-\delta}$ Fuel Cells. *Fuel Cells* **2013**, *13*, 584–591. [\[CrossRef\]](#)
48. Oda, H.; Okuyama, Y.; Sakai, T.; Matsumoto, H. Preparation of Nano-structured $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ cathode for protonic ceramic fuel cell by bead-milling method. *Mater. Trans.* **2014**, *55*, 722–727. [\[CrossRef\]](#)
49. Gao, J.; Meng, Y.; Lee, S.; Tong, J.; Brinkman, K.S. Effect of Infiltration of Barium Carbonate Nanoparticles on the Electrochemical Performance of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ Cathodes for Protonic Ceramic Fuel Cells. *JOM* **2019**, *71*, 90–95. [\[CrossRef\]](#)
50. Taillades, G.; Battochi, P.; Taillades, M.; Jones, D.; Rozière, J. Chemically Stable Electrolytes and Advanced Electrode Architectures for Efficient Proton Ceramic Fuel Cells. *Ecs Trans.* **2019**, *35*, 805–811. [\[CrossRef\]](#)
51. Dailly, J.; Mauvy, F.; Marrony, M.; Pouchard, M.; Grenier, J.-C. Electrochemical properties of perovskite and A_2MO_4 -type oxides used as cathodes in protonic ceramic half cells. *J. Solid State Electrochem.* **2011**, *15*, 245–251. [\[CrossRef\]](#)
52. Lim, D.-K.; Im, H.-N.; Singh, B.; Song, S.-J. Investigations on Electrochemical Performance of a Proton-Conducting Ceramic-Electrolyte Fuel Cell with $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ Cathode. *J. Electrochem. Soc.* **2015**, *162*, F547–F554. [\[CrossRef\]](#)
53. Lim, D.K.; Kim, J.H.; Chavan, A.U.; Lee, T.R.; Yoo, Y.S.; Song, S.J. Performance of proton-conducting ceramic-electrolyte fuel cell with BZCY40 electrolyte and BSCF5582 cathode. *Ceram. Int.* **2016**, *42*, 3776–3785. [\[CrossRef\]](#)
54. Kravchyk, K.V.; Quarez, E.; Solís, C.; Serra, J.M.; Joubert, O. Cathode materials for $\text{La}_{0.995}\text{Ca}_{0.005}\text{NbO}_4$ proton ceramic electrolyte. *Int. J. Hydrog. Energy* **2011**, *36*, 13059–13066. [\[CrossRef\]](#)
55. Quarez, E.; Kravchyk, K.V.; Joubert, O. Compatibility of proton conducting $\text{La}_6\text{WO}_{12}$ electrolyte with standard cathode materials. *Solid State Ion.* **2012**, *216*, 19–24. [\[CrossRef\]](#)
56. Shang, M.; Tong, J.; O'Hayre, R. A promising cathode for intermediate temperature protonic ceramic fuel cells: $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.2}\text{O}_{3-\delta}$. *RSC Adv.* **2013**, *3*, 15769–15775. [\[CrossRef\]](#)
57. Zhang, L.; Yang, S.; Zhang, S.; Yang, Y. Cerium and Gadolinium co-doped perovskite oxide for a protonic ceramic fuel cell cathode. *Int. J. Hydrog. Energy* **2019**, *44*, 27921–27929. [\[CrossRef\]](#)
58. Tolchard, J.; Grande, T. Physicochemical compatibility of SrCeO_3 with potential SOFC cathodes. *J. Solid State Chem.* **2007**, *180*, 2808–2815. [\[CrossRef\]](#)
59. Tolchard, J.R.; Grande, T. Chemical compatibility of candidate oxide cathodes for BaZrO_3 electrolytes. *Solid State Ion.* **2007**, *178*, 593–599. [\[CrossRef\]](#)
60. Yamaura, H.; Ikuta, T.; Yahiro, H.; Okada, G. Cathodic polarization of strontium-doped lanthanum ferrite in proton-conducting solid oxide fuel cell. *Solid State Ion.* **2005**, *176*, 269–274. [\[CrossRef\]](#)
61. Yuan, R.H.; He, W.; Zhang, C.; Ni, M. Cobalt free $\text{SrFe}_{0.95}\text{Nb}_{0.05}\text{O}_{3-\delta}$ cathode material for proton-conducting solid oxide fuel cells with $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ electrolyte. *Mater. Lett.* **2017**, *200*, 75–78. [\[CrossRef\]](#)
62. Ding, H.; Lin, B.; Liu, X.; Meng, G. High performance protonic ceramic membrane fuel cells (PCMFCs) with $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Zn}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ perovskite cathode. *Electrochem. Commun.* **2008**, *10*, 1388–1391. [\[CrossRef\]](#)

63. Lyagaeva, J.; Danilov, N.; Tarutin, A.; Vdovin, G.; Medvedev, D.; Demin, A.; Tsiakaras, P. Designing a protonic ceramic fuel cell with novel electrochemically active oxygen electrodes based on doped $\text{Nd}_{0.5}\text{Ba}_{0.5}\text{FeO}_{3-\delta}$. *Dalt. Trans.* **2018**, *47*, 8149–8157. [\[CrossRef\]](#)
64. Kim, J.H.; Manthiram, A. Low thermal expansion $\text{RBa}(\text{Co},\text{M})_4\text{O}_7$ cathode materials based on tetrahedral-site cobalt ions for solid oxide fuel cells. *Chem. Mater.* **2010**, *22*, 822–831. [\[CrossRef\]](#)
65. Shao, Q.; Ge, W.; Lu, X.; Chen, Y.; Ding, Y.; Lin, B.; Ling, Y. A promising cathode for proton-conducting intermediate temperature solid oxide fuel cells: $\text{Y}_{0.8}\text{Ca}_{0.2}\text{BaCo}_4\text{O}_{7+\delta}$. *Ceram. Int.* **2015**, *41*, 6687–6692. [\[CrossRef\]](#)
66. Medvedev, D.; Lyagaeva, J.; Vdovin, G.; Beresnev, S.; Demin, A.; Tsiakaras, P. A tape calendering method as an effective way for the preparation of proton ceramic fuel cells with enhanced performance. *Electrochim. Acta* **2016**, *210*, 681–688. [\[CrossRef\]](#)
67. Li, S.; Funahashi, R.; Matsubara, I.; Ueno, K.; Sodeoka, S.; Yamada, H. Synthesis and thermoelectric properties of the new oxide materials $\text{Ca}_{(3-x)}\text{Bi}_{(x)}\text{Co}_4\text{O}_{(9-\delta)}$ ($0.0 < x < 0.75$). *Chem. Mater.* **2000**, *12*, 2424–2427. [\[CrossRef\]](#)
68. Yahia, H.B.; Mauvy, F.; Grenier, J.C. $\text{Ca}_{3-x}\text{La}_x\text{Co}_4\text{O}_{9+\delta}$ ($x=0, 0.3$): New cobaltite materials as cathodes for proton conducting solid oxide fuel cell. *J. Solid State Chem.* **2010**, *183*, 527–531. [\[CrossRef\]](#)
69. Pikalova, E.; Kolchugin, A.; Koroleva, M.; Vdovin, G.; Farlenkov, A.; Medvedev, D. Functionality of an oxygen $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ electrode for reversible solid oxide electrochemical cells based on proton-conducting electrolytes. *J. Power Sources* **2019**, *438*, 226996. [\[CrossRef\]](#)
70. Kim, J.H.; Manthiram, A. Layered $\text{LnBaCo}_2\text{O}_{5+\delta}$ perovskite cathodes for solid oxide fuel cells: An overview and perspective. *J. Mater. Chem. A* **2015**, *3*, 24195–24210. [\[CrossRef\]](#)
71. Ding, P.; Li, W.; Zhao, H.; Wu, C.; Zhao, L.; Dong, B.; Wang, S. Review on Ruddlesden-Popper perovskites as cathode for solid oxide fuel cells. *J. Phys. Mater.* **2021**, *4*, 22002. [\[CrossRef\]](#)
72. Pérez-Coll, D.; Heras-Juaristi, G.; Fagg, D.P.; Mather, G.C. Transport-number determination of a protonic ceramic electrolyte membrane via electrode-polarisation correction with the Gorelov method. *J. Power Sources* **2014**, *245*, 445–455. [\[CrossRef\]](#)
73. Frade, J.R. Theoretical behaviour of concentration cells based on ABO_3 perovskite materials with protonic and oxygen ion conduction. *Solid State Ion.* **1995**, *78*, 87–97. [\[CrossRef\]](#)
74. Baek, H.-D. Modeling of electrical conductivity in high-temperature proton-conducting oxides. *Solid State Ion.* **1998**, *110*, 255–262. [\[CrossRef\]](#)
75. Heras-Juaristi, G.; Pérez-Coll, D.; Mather, G.C. Temperature dependence of partial conductivities of the $\text{BaZr}_{0.7}\text{Ce}_{0.2}\text{Y}_{0.1}\text{O}_{3-\delta}$ proton conductor. *J. Power Sources* **2017**, *364*, 52–60. [\[CrossRef\]](#)
76. Fontaine, M.L.; Larring, Y.; Haugsrud, R.; Norby, T.; Wiik, K.; Bredesen, R. Novel high temperature proton conducting fuel cells: Production of $\text{La}_{0.995}\text{Sr}_{0.005}\text{NbO}_{4-\delta}$ electrolyte thin films and compatible cathode architectures. *J. Power Sources* **2009**, *188*, 106–113. [\[CrossRef\]](#)
77. Taillades, G.; Dailly, J.; Taillades-Jacquín, M.; Mauvy, F.; Essouhmi, A.; Marrony, M.; Lalanne, C.; Fourcade, S.; Jones, D.J.; Grenier, J.C.; et al. Intermediate temperature anode-supported fuel cell based on $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_3$ electrolyte with novel Pr_2NiO_4 cathode. *Fuel Cells* **2010**, *10*, 166–173. [\[CrossRef\]](#)
78. Dailly, J.; Fourcade, S.; Largeteau, A.; Mauvy, F.; Grenier, J.C.; Marrony, M. Perovskite and A_2MO_4 -type oxides as new cathode materials for protonic solid oxide fuel cells. *Electrochim. Acta* **2010**, *55*, 5847–5853. [\[CrossRef\]](#)
79. Dailly, J.; Marrony, M. BCY-based proton conducting ceramic cell: 1000 h of long term testing in fuel cell application. *J. Power Sources* **2013**, *240*, 323–327. [\[CrossRef\]](#)
80. Grimaud, A.; Mauvy, F.; Bassat, J.M.; Fourcade, S.; Rocheron, L.; Marrony, M.; Grenier, J.C. Hydration Properties and Rate Determining Steps of the Oxygen Reduction Reaction of Perovskite-Related Oxides as H^+ -SOFC Cathodes. *J. Electrochem. Soc.* **2012**, *159*, B683–B694. [\[CrossRef\]](#)
81. Grimaud, A.; Mauvy, F.; Marc Bassat, J.; Fourcade, S.; Marrony, M.; Claude Grenier, J. Hydration and transport properties of the $\text{Pr}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ compounds as H^+ -SOFC cathodes. *J. Mater. Chem.* **2012**, *22*, 16017. [\[CrossRef\]](#)
82. An, H.; Shin, D.; Ji, H.I. $\text{Pr}_2\text{NiO}_{4+\delta}$ for cathode in protonic ceramic fuel cells. *J. Korean Ceram. Soc.* **2018**, *55*, 358–363. [\[CrossRef\]](#)
83. Tarutin, A.; Kasyanova, A.; Lyagaeva, J.; Vdovin, G.; Medvedev, D. Towards high-performance tubular-type protonic ceramic electrolysis cells with all-Ni-based functional electrodes. *J. Energy Chem.* **2020**, *40*, 65–74. [\[CrossRef\]](#)
84. Tarutin, A.P.; Gorshkov, M.Y.; Bainov, I.N.; Vdovin, G.K.; Vylkov, A.I.; Lyagaeva, J.G.; Medvedev, D.A. Barium-doped nickelates $\text{Nd}_{2-x}\text{Ba}_x\text{NiO}_{4+\delta}$ as promising electrode materials for protonic ceramic electrochemical cells. *Ceram. Int.* **2020**, *46*, 24355–24364. [\[CrossRef\]](#)
85. Tarutin, A.P.; Vdovin, G.K.; Medvedev, D.A.; Yaremchenko, A.A. Fluorine-containing oxygen electrodes of the nickelate family for proton-conducting electrochemical cells. *Electrochim. Acta* **2020**, *337*. [\[CrossRef\]](#)
86. Miao, L.; Hou, J.; Gong, Z.; Jin, Z.; Liu, W. A high-performance cobalt-free Ruddlesden-Popper phase cathode $\text{La}_{1.2}\text{Sr}_{0.8}\text{Ni}_{0.6}\text{Fe}_{0.4}\text{O}_{4+\delta}$ for low temperature proton-conducting solid oxide fuel cells. *Int. J. Hydrog. Energy* **2019**, *44*, 7531–7537. [\[CrossRef\]](#)
87. Gu, C.Y.; Wu, X.S.; Cao, J.F.; Hou, J.; Miao, L.N.; Xia, Y.P.; Liu, W. High performance Ca-containing $\text{La}_{2-x}\text{Ca}_x\text{NiO}_{4+\delta}$ ($0 \leq x \leq 0.75$) cathode for proton-conducting solid oxide fuel cells. *Int. J. Hydrog. Energy* **2020**, *45*, 23422–23432. [\[CrossRef\]](#)
88. Chen, Z.; Wang, J.; Huan, D.; Sun, S.; Wang, G.; Fu, Z.; Zhang, W.; Zheng, X.; Pan, H.; Peng, R.; et al. Tailoring the activity via cobalt doping of a two-layer Ruddlesden-Popper phase cathode for intermediate temperature solid oxide fuel cells. *J. Power Sources* **2017**, *371*, 41–47. [\[CrossRef\]](#)

89. Wang, J.; Zhou, J.; Wang, T.; Chen, G.; Wu, K.; Cheng, Y. Decreasing the polarization resistance of LaSrCoO₄ cathode by Fe substitution for Ba(Zr_{0.1}Ce_{0.7}Y_{0.2})O₃-based protonic ceramic fuel cells. *J. Alloy. Compd.* **2016**, *689*, 581–586. [\[CrossRef\]](#)
90. Tang, H.; Jin, Z.; Wu, Y.; Liu, W.; Bi, L. Cobalt-free nanofiber cathodes for proton conducting solid oxide fuel cells. *Electrochem. Commun.* **2019**, *100*, 108–112. [\[CrossRef\]](#)
91. Zhang, L.; Yang, J.; Li, J. A novel composite cathode for intermediate temperature solid oxide fuel cell. *J. Power Sources* **2014**, *269*, 723–726. [\[CrossRef\]](#)
92. Fan, L.; Su, P.C. Layer-structured LiNi_{0.8}Co_{0.2}O₂: A new triple (H⁺/O²⁻/e⁻) conducting cathode for low temperature proton conducting solid oxide fuel cells. *J. Power Sources* **2016**, *306*, 369–377. [\[CrossRef\]](#)
93. Batocchi, P.; Mauvy, F.; Fourcade, S.; Parco, M. Electrical and electrochemical properties of architected electrodes based on perovskite and A₂MO₄-type oxides for Protonic Ceramic Fuel Cell. *Electrochim. Acta* **2014**, *145*, 1–10. [\[CrossRef\]](#)
94. Lin, B.; Zhang, S.; Zhang, L.; Bi, L.; Ding, H.; Liu, X.; Gao, J.; Meng, G. Protonic ceramic membrane fuel cells with layered GdBaCo₂O_{5+δ} cathode prepared by gel-casting and suspension spray. *J. Power Sources* **2008**, *177*, 330–333. [\[CrossRef\]](#)
95. Lin, B.; Dong, Y.; Yan, R.; Zhang, S.; Hu, M.; Zhou, Y.; Meng, G. In situ screen-printed BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-δ} electrolyte-based protonic ceramic membrane fuel cells with layered SmBaCo₂O_{5+δ} cathode. *J. Power Sources* **2009**, *186*, 446–449. [\[CrossRef\]](#)
96. Ding, H.; Xue, X.; Liu, X.; Meng, G. A novel layered perovskite cathode for proton conducting solid oxide fuel cells. *J. Power Sources* **2010**, *195*, 775–778. [\[CrossRef\]](#)
97. Ling, Y.; Lin, B.; Zhao, L.; Zhang, X.; Yu, J.; Peng, R.; Meng, G.; Liu, X. Layered perovskite LaBaCuMO_{5+δ} (M = Fe, Co) cathodes for intermediate-temperature protonic ceramic membrane fuel cells. *J. Alloy. Compd.* **2010**, *493*, 252–255. [\[CrossRef\]](#)
98. Kim, J.; Sengodan, S.; Kwon, G.; Ding, D.; Shin, J.; Liu, M.; Kim, G. Triple-Conducting Layered Perovskites as Cathode Materials for Proton-Conducting Solid Oxide Fuel Cells. *ChemSusChem* **2014**, *7*, 2811–2815. [\[CrossRef\]](#)
99. Strandbakke, R.; Cherepanov, V.A.; Zuev, A.Y.; Tsvetkov, D.S.; Argiris, C.; Sourkouni, G.; Prünke, S.; Norby, T. Gd- and Pr-based double perovskite cobaltites as oxygen electrodes for proton ceramic fuel cells and electrolyser cells. *Solid State Ion.* **2015**, *278*, 120–132. [\[CrossRef\]](#)
100. Briec, F.; Dezanee, G.; Hayoun, M.; Dammak, H. Proton diffusion mechanisms in the double perovskite cathode material GdBaCo₂O_{5.5}: A molecular dynamics study. *Solid State Ion.* **2017**, *309*, 187–191. [\[CrossRef\]](#)
101. Choi, S.; Kucharczyk, C.J.; Liang, Y.; Zhang, X.; Takeuchi, I.; Ji, H.I.; Haile, S.M. Exceptional power density and stability at intermediate temperatures in protonic ceramic fuel cells. *Nat. Energy* **2018**, *3*, 202–210. [\[CrossRef\]](#)
102. Choi, S.; Davenport, T.C.; Haile, S.M. Protonic ceramic electrochemical cells for hydrogen production and electricity generation: Exceptional reversibility, stability, and demonstrated faradaic efficiency. *Energy Environ. Sci.* **2019**, *12*, 206–215. [\[CrossRef\]](#)
103. Kang, E.H.; Choi, H.R.; Park, J.S.; Kim, K.H.; Kim, D.H.; Bae, K.; Prinz, F.B.; Shim, J.H. Protonic ceramic fuel cells with slurry-spin coated BaZr_{0.2}Ce_{0.6}Y_{0.1}Yb_{0.1}O_{3-δ} thin-film electrolytes. *J. Power Sources* **2020**, *465*, 228254. [\[CrossRef\]](#)
104. Bernuy-Lopez, C.; Rioja-Monllor, L.; Nakamura, T.; Ricote, S.; O'Hayre, R.; Amezcua, K.; Einarsrud, M.A.; Grande, T. Effect of cation ordering on the performance and chemical stability of layered double perovskite cathodes. *Materials* **2018**, *11*, 196. [\[CrossRef\]](#) [\[PubMed\]](#)
105. Tang, W.; Ding, H.; Bian, W.; Wu, W.; Li, W.; Liu, X.; Gomez, J.Y.; Regalado Vera, C.Y.; Zhou, M.; Ding, D. Understanding of A-site deficiency in layered perovskites: Promotion of dual reaction kinetics for water oxidation and oxygen reduction in protonic ceramic electrochemical cells. *J. Mater. Chem. A* **2020**, *8*, 14600–14608. [\[CrossRef\]](#)
106. Zhou, C.; Sunarso, J.; Song, Y.; Dai, J.; Zhang, J.; Gu, B.; Zhou, W.; Shao, Z. New reduced-temperature ceramic fuel cells with dual-ion conducting electrolyte and triple-conducting double perovskite cathode. *J. Mater. Chem. A* **2019**, *7*, 13265–13274. [\[CrossRef\]](#)
107. Zhang, X.; Jiang, Y.; Hu, X.; Sun, L.; Ling, Y. High Performance Proton-Conducting Solid Oxide Fuel Cells with a Layered Perovskite GdBaCuCoO_{5+δ} Cathode. *Electron. Mater. Lett.* **2018**, *14*, 147–153. [\[CrossRef\]](#)
108. Wang, Q.; Hou, J.; Fan, Y.; Xi, X.A.; Li, J.; Lu, Y.; Huo, G.; Shao, L.; Fu, X.Z.; Luo, J.L. Pr₂Ba₂NiMnO_{7-δ} double-layered Ruddlesden-Popper perovskite oxides as efficient cathode electrocatalysts for low temperature proton conducting solid oxide fuel cells. *J. Mater. Chem. A* **2020**, *8*, 7704–7712. [\[CrossRef\]](#)
109. Grimaud, A.; Bassat, J.M.; Mauvy, F.; Pollet, M.; Wattiaux, A.; Marrony, M.; Grenier, J.C. Oxygen reduction reaction of PrBaCo_{2-x}Fe_xO_{5+δ} compounds as H⁺-SOFC cathodes: Correlation with physical properties. *J. Mater. Chem. A* **2014**, *2*, 3594–3604. [\[CrossRef\]](#)
110. Téllez Lozano, H.; Druce, J.; Cooper, S.J.; Kilner, J.A. Double perovskite cathodes for proton-conducting ceramic fuel cells: Are they triple mixed ionic electronic conductors? *Sci. Technol. Adv. Mater.* **2017**, *18*, 977–986. [\[CrossRef\]](#)
111. Malyshkin, D.; Novikov, A.; Ivanov, I.; Sereda, V.; Tsvetkov, D.; Zuev, A. The origin of triple conductivity and water uptake in layered double perovskites: A case study on lanthanum-substituted GdBaCo₂O_{6-δ}. *J. Alloy. Compd.* **2020**, *845*, 156309. [\[CrossRef\]](#)
112. Leonard, K.; Druce, J.; Thoretton, V.; Kilner, J.A.; Matsumoto, H. Exploring mixed proton/electron conducting air electrode materials in protonic electrolysis cell. *Solid State Ion.* **2018**, *319*, 218–222. [\[CrossRef\]](#)
113. Vøllestad, E.; Strandbakke, R.; Tarach, M.; Catalán-Martínez, D.; Fontaine, M.L.; Beeaff, D.; Clark, D.R.; Serra, J.M.; Norby, T. Mixed proton and electron conducting double perovskite anodes for stable and efficient tubular proton ceramic electrolyzers. *Nat. Mater.* **2019**, *18*, 752–759. [\[CrossRef\]](#) [\[PubMed\]](#)

114. Ding, H.; Wu, W.; Jiang, C.; Ding, Y.; Bian, W.; Hu, B.; Singh, P.; Orme, C.J.; Wang, L.; Zhang, Y.; et al. Self-sustainable protonic ceramic electrochemical cells using a triple conducting electrode for hydrogen and power production. *Nat. Commun.* **2020**, *11*. [[CrossRef](#)] [[PubMed](#)]
115. Duan, C.; Tong, J.; Shang, M.; Nikodemski, S.; Sanders, M.; Ricote, S.; Almansoori, A.; O'Hayre, R. Readily processed protonic ceramic fuel cells with high performance at low temperatures. *Science* **2015**, *349*, 1321–1326. [[CrossRef](#)]
116. Duan, C.; Hook, D.; Chen, Y.; Tong, J.; O'Hayre, R. Zr and Y co-doped perovskite as a stable, high performance cathode for solid oxide fuel cells operating below 500 °C. *Energy Environ. Sci.* **2017**, *10*, 176–182. [[CrossRef](#)]
117. Dubois, A.; Ricote, S.; Braun, R.J. Benchmarking the expected stack manufacturing cost of next generation, intermediate-temperature protonic ceramic fuel cells with solid oxide fuel cell technology. *J. Power Sources* **2017**, *369*, 65–77. [[CrossRef](#)]
118. Ren, R.; Wang, Z.; Xu, C.; Sun, W.; Qiao, J.; Rooney, D.W.; Sun, K. Tuning the defects of the triple conducting oxide $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$ perovskite toward enhanced cathode activity of protonic ceramic fuel cells. *J. Mater. Chem. A* **2019**, *7*, 18365–18372. [[CrossRef](#)]
119. He, F.; Liang, M.; Wang, W.; Ran, R.; Yang, G.; Zhou, W.; Shao, Z. High-Performance Proton-Conducting Fuel Cell with B-Site-Deficient Perovskites for All Cell Components. *Energy Fuels* **2020**, *34*, 11464–11471. [[CrossRef](#)]
120. Li, J.; Hou, J.; Lu, Y.; Wang, Q.; Xi, X.; Fan, Y.; Fu, X.Z.; Luo, J.L. Ca-containing $\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Co}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$ cathode with high CO_2 -poisoning tolerance for proton-conducting solid oxide fuel cells. *J. Power Sources* **2020**, *453*, 227909. [[CrossRef](#)]
121. Liang, M.; He, F.; Zhou, C.; Chen, Y.; Ran, R.; Yang, G. Nickel-doped $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$ as a new high-performance cathode for both oxygen-ion and proton conducting fuel cells. *Chem. Eng. J.* **2020**, 127717. [[CrossRef](#)]
122. Zohourian, R.; Merkle, R.; Maier, J. Proton uptake into the protonic cathode material $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.2}\text{O}_{3-\delta}$ and comparison to protonic electrolyte materials. *Solid State Ion.* **2017**, *299*, 64–69. [[CrossRef](#)]
123. Zohourian, R.; Merkle, R.; Raimondi, G.; Maier, J. Mixed-Conducting Perovskites as Cathode Materials for Protonic Ceramic Fuel Cells: Understanding the Trends in Proton Uptake. *Adv. Funct. Mater.* **2018**, *28*, 1801241. [[CrossRef](#)]
124. Chen, Y.; Hong, T.; Wang, P.; Brinkman, K.; Tong, J.; Cheng, J. Investigate the proton uptake process of proton/oxygen ion/hole triple conductor $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$ by electrical conductivity relaxation. *J. Power Sources* **2019**, *440*, 227122. [[CrossRef](#)]
125. Xia, Y.; Jin, Z.; Wang, H.; Gong, Z.; Lv, H.; Peng, R.; Liu, W.; Bi, L. A novel cobalt-free cathode with triple-conduction for proton-conducting solid oxide fuel cells with unprecedented performance. *J. Mater. Chem. A* **2019**, *7*, 16136–16148. [[CrossRef](#)]
126. Dusastre, V.; Kilner, J.A. Optimisation of composite cathodes for intermediate temperature SOFC applications. *Solid State Ion.* **1999**, *126*, 163–174. [[CrossRef](#)]
127. Wu, T.; Peng, R.; Xia, C. $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ - $\text{BaCe}_{0.8}\text{Sm}_{0.2}\text{O}_{3-\delta}$ composite cathodes for proton-conducting solid oxide fuel cells. *Solid State Ion.* **2008**, *179*, 1505–1508. [[CrossRef](#)]
128. Ding, H.; Xue, X.; Liu, X.; Meng, G. High performance protonic ceramic membrane fuel cells (PCMFCs) with $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ perovskite cathode. *J. Alloy. Compd.* **2010**, *494*, 233–235. [[CrossRef](#)]
129. Dailly, J.; Taillades, G.; Ancelin, M.; Pers, P.; Marrony, M. High performing $\text{BaCe}_{0.8}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$ - $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ based protonic ceramic fuel cell. *J. Power Sources* **2017**, *361*, 221–226. [[CrossRef](#)]
130. Dai, H.; Da'as, E.H.; Shafi, S.P.; Wang, H.; Bi, L. Tailoring cathode composite boosts the performance of proton-conducting SOFCs fabricated by a one-step co-firing method. *J. Eur. Ceram. Soc.* **2018**, *38*, 2903–2908. [[CrossRef](#)]
131. Park, S.; Lee, S.; Baek, H.; Shin, D. Cell performance enhancement facilitated by mixed ionic and electronic conductor fiber for protonic ceramic fuel cells. *J. Electroceramics* **2020**, 11–13. [[CrossRef](#)]
132. Bi, L.; Shafi, S.P.; Da'as, E.H.; Traversa, E. Tailoring the Cathode–Electrolyte Interface with Nanoparticles for Boosting the Solid Oxide Fuel Cell Performance of Chemically Stable Proton-Conducting Electrolytes. *Small* **2018**, *14*, 1–9. [[CrossRef](#)] [[PubMed](#)]
133. He, F.; Wu, T.; Peng, R.; Xia, C. Cathode reaction models and performance analysis of $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ - $\text{BaCe}_{0.8}\text{Sm}_{0.2}\text{O}_{3-\delta}$ composite cathode for solid oxide fuel cells with proton conducting electrolyte. *J. Power Sources* **2009**, *194*, 263–268. [[CrossRef](#)]
134. Zhang, Q.; Guo, Y.; Ding, J.; Jiang, G. New approaches for the determination of electrochemical parameters in the model of proton-conducting solid oxide fuel cell. *Electrochim. Acta* **2019**, *318*, 560–571. [[CrossRef](#)]
135. Zhang, Q.; Guo, Y.; Ding, J.; He, M. Modeling investigation of $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ - $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ cathode for proton-conducting ceramic fuel cell. *J. Solid State Electrochem.* **2020**, *24*, 1487–1495. [[CrossRef](#)]
136. Lv, X.; Chen, H.; Zhou, W.; Li, S.D.; Shao, Z. A CO_2 -tolerant $\text{SrCo}_{0.8}\text{Fe}_{0.15}\text{Zr}_{0.05}\text{O}_{3-\delta}$ cathode for proton-conducting solid oxide fuel cells. *J. Mater. Chem. A* **2020**, *8*, 11292–11301. [[CrossRef](#)]
137. Bu, Y.; Joo, S.; Zhang, Y.; Wang, Y.; Meng, D.; Ge, X.; Kim, G. A highly efficient composite cathode for proton-conducting solid oxide fuel cells. *J. Power Sources* **2020**, *451*, 227812. [[CrossRef](#)]
138. Ricote, S.; Bonanos, N.; Lenrick, F.; Wallenberg, R. LaCoO_3 : Promising cathode material for protonic ceramic fuel cells based on a $\text{BaCe}_{0.2}\text{Zr}_{0.7}\text{Y}_{0.1}\text{O}_{3-\delta}$ electrolyte. *J. Power Sources* **2012**, *218*, 313–319. [[CrossRef](#)]
139. Matsui, T.; Manriki, K.; Miyazaki, K.; Muroyama, H.; Eguchi, K. A new oxygen reduction electrocatalyst of barium lanthanide cobaltate for composite cathodes of proton-conducting ceramic fuel cells. *J. Mater. Chem. A* **2018**, *6*, 14188–14194. [[CrossRef](#)]
140. Rioja-Monllor, L.; Bernuy-Lopez, C.; Fontaine, M.L.; Grande, T.; Einarsrud, M.A. Processing of high performance composite cathodes for protonic ceramic fuel cells by exsolution. *J. Mater. Chem. A* **2019**, *7*, 8609–8619. [[CrossRef](#)]
141. Rioja-Monllor, L.; Bernuy-Lopez, C.; Fontaine, M.L.; Grande, T.; Einarsrud, M.A. Compositional engineering of a $\text{La}_{1-x}\text{Ba}_x\text{CoO}_{3-\delta}$ - $(1-a)\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$ ($a = 0.6, 0.7, 0.8$ and $x = 0.5, 0.6, 0.7$) nanocomposite cathodes for protonic ceramic fuel cells. *Materials* **2019**, *12*, 3441. [[CrossRef](#)]

142. Shao, L.; Si, F.; Fu, X.Z.; Luo, J.L. Stable $\text{SrCo}_{0.7}\text{Fe}_{0.2}\text{Zr}_{0.1}\text{O}_{3-\delta}$ cathode material for proton conducting solid oxide fuel cell reactors. *Int. J. Hydrog. Energy* **2018**, *43*, 7511–7514. [\[CrossRef\]](#)
143. Fabbri, E.; Licocchia, S.; Traversa, E.; Wachsmann, E.D. Composite cathodes for proton conducting electrolytes. *Fuel Cells* **2009**, *9*, 128–138. [\[CrossRef\]](#)
144. Yoo, C.Y.; Yun, D.S.; Park, S.Y.; Park, J.; Joo, J.H.; Park, H.; Kwak, M.; Yu, J.H. Investigation of Electrochemical Properties of Model Lanthanum Strontium Cobalt Ferrite-Based Cathodes for Proton Ceramic Fuel Cells. *Electrocatalysis* **2016**, *7*, 280–286. [\[CrossRef\]](#)
145. Lee, S.; Park, S.; Wee, S.; Baek, H.W.; Shin, D. One-dimensional structured $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ - $\text{BaCe}_{0.5}\text{Zr}_{0.35}\text{Y}_{0.15}\text{O}_{3-\delta}$ composite cathode for protonic ceramic fuel cells. *Solid State Ion.* **2018**, *320*, 347–352. [\[CrossRef\]](#)
146. Cui, J.; Wang, J.; Zhang, X.; Li, G.; Wu, K.; Cheng, Y.; Zhou, J. Enhanced oxygen reduction reaction through Ca and Co Co-doped YFeO_3 as cathode for protonic ceramic fuel cells. *J. Power Sources* **2019**, *413*, 148–157. [\[CrossRef\]](#)
147. Shimada, H.; Yamaguchi, Y.; Sumi, H.; Mizutani, Y. Performance Comparison of Perovskite Composite Cathodes with $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ in Anode-Supported Protonic Ceramic Fuel Cells. *J. Electrochem. Soc.* **2020**, *167*, 124506. [\[CrossRef\]](#)
148. Lin, B.; Ding, H.; Dong, Y.; Wang, S.; Zhang, X.; Fang, D.; Meng, G. Intermediate-to-low temperature protonic ceramic membrane fuel cells with $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ - $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ composite cathode. *J. Power Sources* **2009**, *186*, 58–61. [\[CrossRef\]](#)
149. Taillades, G.; Pers, P.; Batocchi, P.; Taillades, M. Advanced Electrodes for Intermediate Temperature Proton Conducting Fuel Cell. *Ecs Trans.* **2013**, *57*, 1289–1296. [\[CrossRef\]](#)
150. Taillades, G.; Pers, P.; Mao, V.; Taillades, M. High performance anode-supported proton ceramic fuel cell elaborated by wet powder spraying. *Int. J. Hydrog. Energy* **2016**, *41*, 12330–12336. [\[CrossRef\]](#)
151. Marrony, M.; Dailly, J. Advanced Proton Conducting Ceramic Cell as Energy Storage Device. *J. Electrochem. Soc.* **2017**, *164*, F988–F994. [\[CrossRef\]](#)
152. Xu, X.; Wang, H.; Fronzi, M.; Wang, X.; Bi, L.; Traversa, E. Tailoring cations in a perovskite cathode for proton-conducting solid oxide fuel cells with high performance. *J. Mater. Chem. A* **2019**, *7*, 20624–20632. [\[CrossRef\]](#)
153. Duan, C.; Kee, R.J.; Zhu, H.; Karakaya, C.; Chen, Y.; Ricote, S.; Jarry, A.; Crumlin, E.J.; Hook, D.; Braun, R.; et al. Highly durable, coking and sulfur tolerant, fuel-flexible protonic ceramic fuel cells. *Nature* **2018**, *557*, 217–222. [\[CrossRef\]](#) [\[PubMed\]](#)
154. dos Santos-Gómez, L.; Zamudio-García, J.; Porras-Vázquez, J.M.; Losilla, E.R.; Marrero-López, D. Nanostructured $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$ cathodes with different microstructural architectures. *Nanomaterials* **2020**, *10*, 1055. [\[CrossRef\]](#) [\[PubMed\]](#)
155. Bi, L.; Zhang, S.; Lin, B.; Fang, S.; Xia, C.; Liu, W. Screen-printed $\text{BaCe}_{0.8}\text{Sm}_{0.2}\text{O}_{3-\delta}$ thin membrane solid oxide fuel cells with surface modification by spray coating. *J. Alloy. Compd.* **2009**, *473*, 48–52. [\[CrossRef\]](#)
156. Song, S.H.; Yoon, S.E.; Choi, J.; Kim, B.K.; Park, J.S. A high-performance ceramic composite anode for protonic ceramic fuel cells based on lanthanum strontium vanadate. *Int. J. Hydrog. Energy* **2014**, *39*, 16534–16540. [\[CrossRef\]](#)
157. Choi, J.; Kim, B.; Song, S.H.; Park, J.S. A composite cathode with undoped LaFeO_3 for protonic ceramic fuel cells. *Int. J. Hydrog. Energy* **2016**, *41*, 9619–9626. [\[CrossRef\]](#)
158. Shin, E.K.; Anggia, E.; Parveen, A.S.; Park, J.S. Optimization of the protonic ceramic composition in composite electrodes for high-performance protonic ceramic fuel cells. *Int. J. Hydrog. Energy* **2019**, *44*, 31323–31332. [\[CrossRef\]](#)
159. Ren, R.; Wang, Z.; Meng, X.; Wang, X.; Xu, C.; Qiao, J.; Sun, W.; Sun, K. Tailoring the Oxygen Vacancy to Achieve Fast Intrinsic Proton Transport in a Perovskite Cathode for Protonic Ceramic Fuel Cells. *ACS Appl. Energy Mater.* **2020**, *3*, 4914–4922. [\[CrossRef\]](#)
160. Lei, L.; Tao, Z.; Wang, X.; Lemmon, J.P.; Chen, F. Intermediate-temperature solid oxide electrolysis cells with thin proton-conducting electrolyte and a robust air electrode. *J. Mater. Chem. A* **2017**, *5*, 22945–22951. [\[CrossRef\]](#)
161. Shin, E.K.; Shin, M.; Lee, H.; Park, J.S. Catalysts for composite cathodes of protonic ceramic fuel cells. *Ceram. Int.* **2018**, *44*, 8423–8426. [\[CrossRef\]](#)
162. Sun, W.; Fang, S.; Yan, L.; Liu, W. Proton-Blocking Composite Cathode for Proton-Conducting Solid Oxide Fuel Cell. *J. Electrochem. Soc.* **2011**, *158*, B1432. [\[CrossRef\]](#)
163. Sun, W.; Zhu, Z.; Jiang, Y.; Shi, Z.; Yan, L.; Liu, W. Optimization of $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ -based proton-conducting solid oxide fuel cells with a cobalt-free proton-blocking $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_{3-\delta}$ - $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ composite cathode. *Int. J. Hydrog. Energy* **2011**, *36*, 9956–9966. [\[CrossRef\]](#)
164. Hou, J.; Zhu, Z.; Qian, J.; Liu, W. A new cobalt-free proton-blocking composite cathode $\text{La}_2\text{NiO}_{4+\delta}$ - $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$ for $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ -based solid oxide fuel cells. *J. Power Sources* **2014**, *264*, 67–75. [\[CrossRef\]](#)
165. Gong, Z.; Hou, J.; Wang, Z.; Cao, J.; Zhang, J.; Liu, W. A new cobalt-free composite cathode $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ - $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ for proton-conducting solid oxide fuel cells. *Electrochim. Acta* **2015**, *178*, 60–64. [\[CrossRef\]](#)
166. Xu, X.; Wang, H.; Ma, J.; Liu, W.; Wang, X.; Fronzi, M.; Bi, L. Impressive performance of proton-conducting solid oxide fuel cells using a first-generation cathode with tailored cations. *J. Mater. Chem. A* **2019**, *7*, 18792–18798. [\[CrossRef\]](#)
167. Vert, V.B.; Solís, C.; Serra, J.M. Electrochemical Properties of PSFC-BCYb Composites as Cathodes for Proton Conducting Solid Oxide Fuel Cells. *Fuel Cells* **2011**, *11*, 81–90. [\[CrossRef\]](#)
168. Shi, H.; Ding, Z.; Ma, G. Electrochemical Performance of Cobalt-free $\text{Nd}_{0.5}\text{Ba}_{0.5}\text{Fe}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ Cathode Materials for Intermediate Temperature Solid Oxide Fuel Cells. *Fuel Cells* **2016**, *16*, 258–262. [\[CrossRef\]](#)
169. Zhao, Z.; Cui, J.; Zou, M.; Mu, S.; Huang, H.; Meng, Y.; He, K.; Brinkman, K.S.; Tong, J. Novel twin-perovskite nanocomposite of Ba–Ce–Fe–Co–O as a promising triple conducting cathode material for protonic ceramic fuel cells. *J. Power Sources* **2020**, *450*, 227609. [\[CrossRef\]](#)

170. Lu, X.; Chen, Y.; Ding, Y.; Lin, B. A cobalt-free $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ - $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ composite cathode for proton-conducting solid oxide fuel cells. *Int. J. Hydrog. Energy* **2012**, *37*, 8630–8634. [\[CrossRef\]](#)
171. Liu, J.; Ding, J.; Miao, L.; Gong, Z.; Li, K.; Liu, W. High performance $\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Fe}_{0.9-x}\text{Sn}_x\text{Y}_{0.1}\text{O}_{3-\delta}$ -SDC as cobalt-free cathode for intermediate-temperature proton-conducting solid oxide fuel cells with $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ electrolyte. *J. Alloy. Compd.* **2019**, *786*, 163–168. [\[CrossRef\]](#)
172. Liu, Y.; Shi, Y.; Wu, C.; Lu, F.; He, H.; Su, J.; Cai, B. Physical properties of $(\text{SrBa})_{1-x}\text{Pr}_x(\text{CuTi})_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ ($x = 0\text{--}1.0$) and its application in H-SOFCs. *Solid State Ion.* **2020**, *348*. [\[CrossRef\]](#)
173. Lin, B.; Wang, S.; Liu, X.; Meng, G. Stable proton-conducting Ca-doped LaNbO_4 thin electrolyte-based protonic ceramic membrane fuel cells by in situ screen printing. *J. Alloy. Compd.* **2009**, *478*, 355–357. [\[CrossRef\]](#)
174. Solís, C.; Vert, V.B.; Fabuel, M.; Serra, J.M. Electrochemical properties of composite cathodes for $\text{La}_{0.995}\text{Ca}_{0.005}\text{NbO}_{4-\delta}$ -based proton conducting fuel cells. *J. Power Sources* **2011**, *196*, 9220–9227. [\[CrossRef\]](#)
175. Solís, C.; Navarrete, L.; Roitsch, S.; Serra, J.M. Electrochemical properties of composite fuel cell cathodes for $\text{La}_{5.5}\text{WO}_{12-\delta}$ proton conducting electrolytes. *J. Mater. Chem.* **2012**, *22*, 16051–16059. [\[CrossRef\]](#)
176. Solís, C.; Navarrete, L.; Bozza, F.; Bonanos, N.; Serra, J.M. Catalytic Surface Promotion of Composite Cathodes in Protonic Ceramic Fuel Cells. *ChemElectroChem* **2015**, *2*, 1106–1110. [\[CrossRef\]](#)
177. Strandbakke, R.; Dyrli, O.; Hage, F.S.; Norby, T. Reaction Kinetics of Protons and Oxide Ions in LSM/Lanthanum Tungstate Cathodes with Pt Nanoparticle Activation. *J. Electrochem. Soc.* **2016**, *163*, F507–F515. [\[CrossRef\]](#)
178. Lee, K.C.; Choi, M.B.; Lim, D.K.; Singh, B.; Song, S.J. Effect of humidification on the performance of intermediate-temperature proton conducting ceramic fuel cells with ceramic composite cathodes. *J. Power Sources* **2013**, *232*, 224–233. [\[CrossRef\]](#)
179. Hou, J.; Wang, Q.; Li, J.; Lu, Y.; Wang, L.; Fu, X.Z.; Luo, J.L. Rational design of an in-situ co-assembly nanocomposite cathode $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_{4+\delta}$ - $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_{3-\delta}$ for lower-temperature proton-conducting solid oxide fuel cells. *J. Power Sources* **2020**, *466*, 228240. [\[CrossRef\]](#)
180. Bausá, N.; Serra, J.M. Robust catalytically-activated LSM-BCZY-based composite steam electrodes for proton ceramic electrolysis cells. *Rsc Adv.* **2019**, *9*, 20677–20686. [\[CrossRef\]](#)
181. Gan, Y.; Zhang, J.; Li, Y.; Li, S.; Kui, X.; Irvine, J.T.S. Composite Oxygen Electrode Based on LSCF and BSCF for Steam Electrolysis in a Proton-Conducting Solid Oxide Electrolyzer. *J. Electrochem. Soc.* **2012**, *160*, F763–F767. [\[CrossRef\]](#)
182. Yang, C.; Zhang, X.; Zhao, H.; Shen, Y.; Du, Z.; Zhang, C. Electrochemical properties of $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ - $\text{Nd}_{1.95}\text{NiO}_{4+\delta}$ composite cathode for protonic ceramic fuel cells. *Int. J. Hydrog. Energy* **2015**, *40*, 2800–2807. [\[CrossRef\]](#)
183. Babiniec, S.M.; Ricote, S.; Sullivan, N.P. Characterization of ionic transport through $\text{BaCe}_{0.2}\text{Zr}_{0.7}\text{Y}_{0.1}\text{O}_{3-\delta}$ membranes in galvanic and electrolytic operation. *Int. J. Hydrog. Energy* **2015**, *40*, 9278–9286. [\[CrossRef\]](#)
184. Li, G.; Jin, H.; Cui, Y.; Gui, L.; He, B.; Zhao, L. Application of a novel $(\text{Pr}_{0.9}\text{La}_{0.1})_2(\text{Ni}_{0.74}\text{Cu}_{0.21}\text{Nb}_{0.05})\text{O}_{4+\delta}$ -infiltrated $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ cathode for high performance protonic ceramic fuel cells. *J. Power Sources* **2017**, *341*, 192–198. [\[CrossRef\]](#)
185. Tarutin, A.; Danilov, N.; Lyagaeva, J.; Medvedev, D. One-step fabrication of protonic ceramic fuel cells using a convenient tape calendering method. *Appl. Sci.* **2020**, *10*, 2481. [\[CrossRef\]](#)
186. Li, W.; Guan, B.; Ma, L.; Hu, S.; Zhang, N.; Liu, X. High performing triple-conductive $\text{Pr}_2\text{NiO}_{4+\delta}$ anode for proton-conducting steam solid oxide electrolysis cell. *J. Mater. Chem. A* **2018**, *6*, 18057–18066. [\[CrossRef\]](#)
187. Tang, H.; Gong, Z.; Wu, Y.; Jin, Z.; Liu, W. Electrochemical performance of nanostructured LNF infiltrated onto LNO cathode for $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ -based solid oxide fuel cell. *Int. J. Hydrog. Energy* **2018**, *43*, 19749–19756. [\[CrossRef\]](#)
188. Pikalova, E.; Kolchugin, A.; Bogdanovich, N.; Medvedev, D.; Lyagaeva, J.; Vedmid', L.; Ananyev, M.; Plaksin, S.; Farlenkov, A. Suitability of $\text{Pr}_{2-x}\text{Ca}_x\text{NiO}_{4+\delta}$ as cathode materials for electrochemical devices based on oxygen ion and proton conducting solid state electrolytes. *Int. J. Hydrog. Energy* **2020**, *45*, 13612–13624. [\[CrossRef\]](#)
189. Huan, D.; Shi, N.; Zhang, L.; Tan, W.; Xie, Y.; Wang, W.; Xia, C.; Peng, R.; Lu, Y. New, Efficient, and Reliable Air Electrode Material for Proton-Conducting Reversible Solid Oxide Cells. *ACS Appl. Mater. Interfaces* **2018**, *10*, 1761–1770. [\[CrossRef\]](#)
190. Park, K.Y.; Kim, Y.D.; Lee, J.I.; Saqib, M.; Shin, J.S.; Seo, Y.; Kim, J.H.; Lim, H.T.; Park, J.Y. Operation Protocols to Improve Durability of Protonic Ceramic Fuel Cells. *ACS Appl. Mater. Interfaces* **2019**, *11*, 457–468. [\[CrossRef\]](#)
191. Xie, D.; Ling, A.; Yan, D.; Jia, L.; Chi, B.; Pu, J.; Li, J. A comparative study on the composite cathodes with proton conductor and oxygen ion conductor for proton-conducting solid oxide fuel cell. *Electrochim. Acta* **2020**, *344*, 136143. [\[CrossRef\]](#)
192. Kim, J.; Jun, A.; Gwon, O.; Yoo, S.; Liu, M.; Shin, J.; Lim, T.H.; Kim, G. Hybrid-solid oxide electrolysis cell: A new strategy for efficient hydrogen production. *Nano Energy* **2018**, *44*, 121–126. [\[CrossRef\]](#)
193. Liu, B.; Jia, L.; Chi, B.; Pu, J.; Li, J. A novel $\text{PrBaCo}_2\text{O}_{5+\delta}$ - $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_3$ composite cathode for proton-conducting solid oxide fuel cells. *Compos. Part. B Eng.* **2020**, *191*, 107936. [\[CrossRef\]](#)
194. Wang, D.; Xia, Y.; Lv, H.; Miao, L.; Bi, L.; Liu, W. $\text{PrBaCo}_{2-x}\text{Ta}_x\text{O}_{5+\delta}$ based composite materials as cathodes for proton-conducting solid oxide fuel cells with high CO_2 resistance. *Int. J. Hydrog. Energy* **2020**, *45*, 31017–31026. [\[CrossRef\]](#)
195. Liu, B.; Yang, J.; Yan, D.; Jia, L.; Chi, B.; Pu, J.; Li, J. Novel $\text{PrBa}_{0.9}\text{Ca}_{0.1}\text{Co}_{2-x}\text{Zn}_x\text{O}_{5+\delta}$ double-perovskite as an active cathode material for high-performance proton-conducting solid oxide fuel cells. *Int. J. Hydrog. Energy* **2020**, *45*, 31009–31016. [\[CrossRef\]](#)
196. Wei, K.; Li, N.; Wu, Y.; Song, W.; Wang, X.; Guo, L.; Khan, M.; Wang, S.; Zhou, F.; Ling, Y. Characterization and optimization of highly active and Ba-deficient $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$ -based cathode materials for protonic ceramics fuel cells. *Ceram. Int.* **2019**, *45*, 18583–18591. [\[CrossRef\]](#)

197. Wang, Z.; Lv, P.; Yang, L.; Guan, R.; Jiang, J.; Jin, F.; He, T. $\text{Ba}_{0.95}\text{La}_{0.05}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{3-\delta}$ cobalt-free perovskite as a triple-conducting cathode for proton-conducting solid oxide fuel cells. *Ceram. Int.* **2020**, *46*, 18216–18223. [[CrossRef](#)]
198. Chen, D.; Zhang, Q.; Lu, L.; Periasamy, V.; Tade, M.O.; Shao, Z. Multi scale and physics models for intermediate and low temperatures H^+ -solid oxide fuel cells with $\text{H}^+/\text{e}^-/\text{O}^{2-}$ mixed conducting properties: Part A, generalized percolation theory for LSCF-SDC-BZCY 3-component cathodes. *J. Power Sources* **2016**, *303*, 305–316. [[CrossRef](#)]
199. Li, G.; Zhang, Y.; Ling, Y.; He, B.; Xu, J.; Zhao, L. Probing novel triple phase conducting composite cathode for high performance protonic ceramic fuel cells. *Int. J. Hydrog. Energy* **2016**, *41*, 5074–5083. [[CrossRef](#)]
200. Tsvetkov, D.; Tsvetkova, N.; Ivanov, I.; Malyshkin, D.; Sereda, V.; Zuev, A. $\text{PrBaCo}_2\text{O}_{6-\delta}\text{-Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ composite cathodes for intermediate-temperature solid oxide fuel cells: Stability and cation interdiffusion. *Energies* **2019**, *12*, 417. [[CrossRef](#)]