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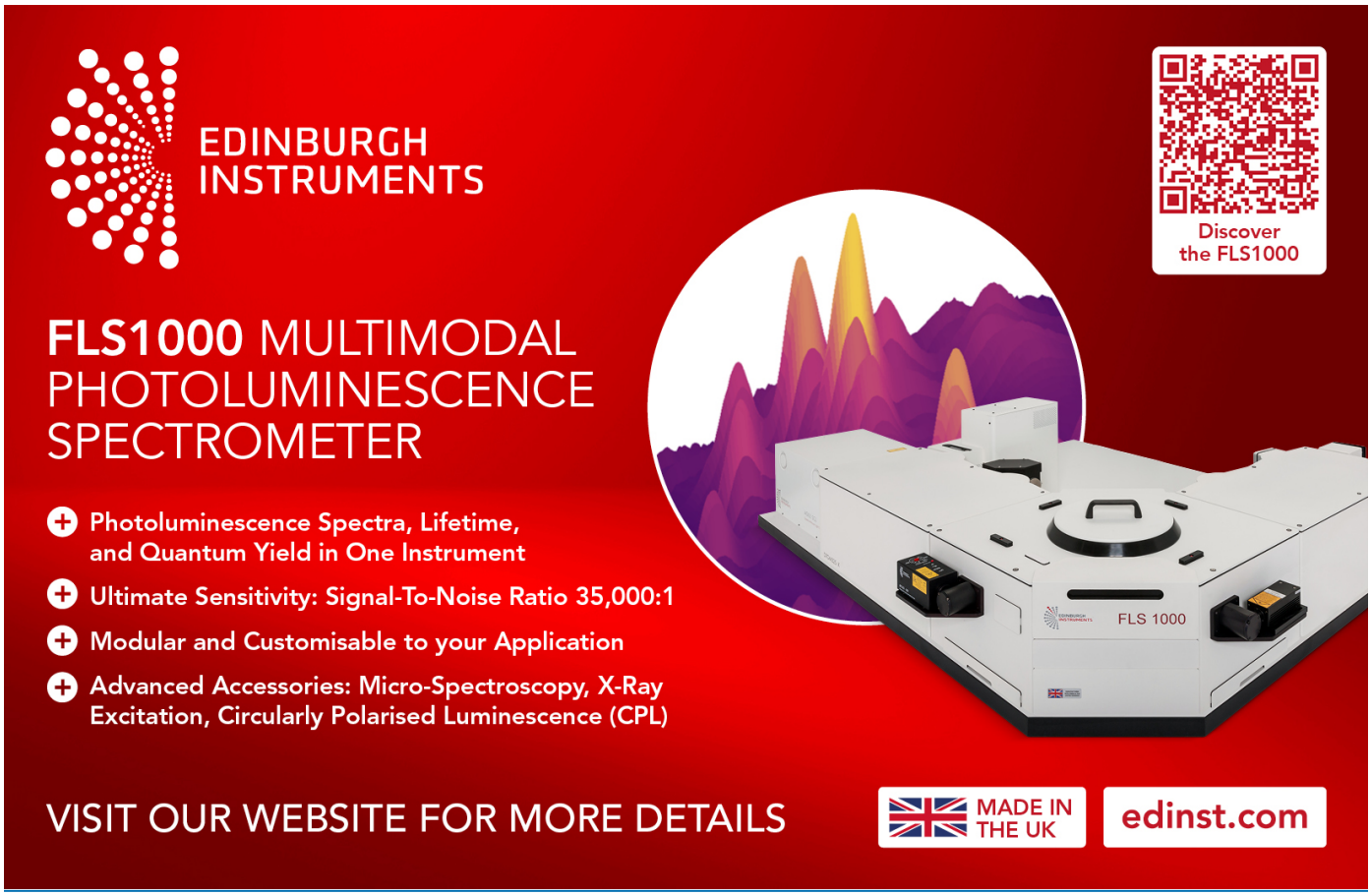
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Topical Review

Advancing electrochemical devices: the promise of triple ionic–electronic conducting oxides

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Abstract

Triple ionic–electronic conducting materials represent a key advancement in the development of electrochemical devices, enabling simultaneous transport of electrons, oxygen ions, and protons. This unique property allows triple ionic–electronic conducting materials to overcome the limitations of traditional mixed ionic–electronic conductors by expanding reaction zones from interfacial regions to the material bulk, significantly enhancing reaction kinetics. Triple ionic–electronic conducting materials have shown promise in devices such as solid oxide fuel cells, protonic ceramic cells, and catalytic membrane reactors, delivering improved efficiency, especially at intermediate temperatures. This review provides a concise examination of properties of triple ionic–electronic conducting materials, focusing on the role of perovskite and layered oxide systems. Key mechanisms of conduction, including proton hopping via the Grotthuss mechanism, oxygen ion diffusion through vacancy pathways, and electronic conduction via small-polaron hopping, are critically analysed. Advances in material design, such as doping strategies to stabilise crystal phases and optimise defect chemistry, are highlighted as crucial enablers of high-performance triple ionic–electronic conducting materials. Despite their promise, triple ionic–electronic conducting materials face challenges related to material degradation, phase instability, and scalability. This review discusses recent innovations aimed at addressing these issues, including multi-phase composites and computational

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modelling for material optimisation. By offering an integrated understanding of triple ionic–electronic conducting materials' fundamental properties, applications, and challenges, this work aims to guide further research, positioning triple ionic–electronic conducting materials as a promising candidate for the next-generation sustainable energy technologies.

Keywords: ionic conductors, electrochemical technologies, mixed ionic–electronic conductors, triple ionic–electronic conductors, materials innovation

1. Introduction

The search for advanced materials that can enhance the performance, efficiency, and sustainability of electrochemical devices has been a basis of modern energy materials research [1–4]. Electrochemical devices, such as fuel cells, electrolysers, and catalytic membrane reactors, are pivotal in achieving efficient energy conversion and storage, particularly in the context of the global transition to sustainable energy systems [5, 6]. Among the materials at the forefront of these efforts are triple ionic–electronic conductors (TIECs), which have emerged as promising candidate materials due to their ability to simultaneously transport electrons, oxygen ions, and protons [7–9]. This remarkable feature distinguishes TIECs from traditional mixed ionic–electronic conductors (MIECs), positioning them as key candidates for next-generation electrochemical technologies [10].

To clarify the forthcoming discussion, distinguishing between solid oxide fuel cells (SOFCs) and protonic ceramic fuel cells (PCFCs) is useful. In SOFCs, the electrolyte conducts oxygen ions, while in PCFCs, it conducts protons. Some electrolytes can transport both species. In a PCFC cathode, the reaction involves holes, protons, and oxygen, making a TIEC cathode a suitable choice. While oxygen-ion transport is not essential, high oxygen reduction reaction (ORR) activity due to faster oxygen transport is crucial [11]. Additionally, it has been shown that the oxygen-ion conduction can enhance the cathode reaction rate through extra bulk and surface transport pathways [12]. TIECs have also been shown to enhance the performance of other solid oxide electrochemical cells. For instance, a $BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$-based cathode improved SOFC performance at intermediate temperatures [13]. While proton conductivity in this context may be unnecessary, it still contributes to high performance through increased mobility of oxygen-vacancy defects and thus contributes to strong ORR activity.

The conventional paradigm in electrochemical devices often relies on MIECs, which support the transport of electrons and one type of ionic species (protons or oxygen ions) [14, 15]. While effective in certain contexts, MIECs are constrained by the necessity of double and triple-phase boundaries (DPB and TPBs), regions where electrons, ions, and reactants coexist [16–18]. These boundaries, typically limited to interfacial areas, restrict the extent of electrochemical reactions, thereby limiting the overall efficiency of the device. The schematic in figure 1(b) shows that, unlike pure electronic or MIECs, TIECs enable distributed charge carrier transport throughout the entire volume of the cathode material. This allows the electrochemical reactions to occur over a broader area, not just confined to the traditional two-phase boundary (2PB) or three-phase boundary (3PB) found in conventional materials. The co-transport of H^+ and O^{2-} in the bulk helps to spatially decouple the charge-transfer steps for hydrogen oxidation and oxygen reduction, enabling extended reaction zones and improved electrode utilisation (figure 1) [10, 19]. For fuel cells, the ability to operate efficiently at intermediate temperatures (400 °C–700 °C) is crucial for addressing challenges associated with high-temperature operation, such as material degradation, sealing complexities, and high manufacturing costs. TIECs, with their unique conduction properties, offer a pathway to achieve high performance under these conditions [20, 21]. In particular, materials such as Ba(Zr, Ce)O_3-based perovskites and layered oxides like $NdBaCo_2O_{5+\delta}$ have demonstrated exceptional potential, achieving enhanced proton and oxygen ion conductivity through strategic doping and defect engineering [22, 23].

Structurally, TIECs are characterised by their perovskite, ABO_3 framework [24]. Perovskite ABO_3 frameworks offer substantial structural flexibility because their A and B sites can accommodate a broad range of cations and anions, a feature long exploited in MIECs to introduce a single mobile ionic species alongside electronic carriers Zr [25–27]. Recent work on TIECs shows that the same lattice can be co-doped on both sites to stabilise protons, oxygen vacancies and electronic holes simultaneously, enabling genuine bulk triple conduction rather than activity restricted to narrow 2PB or 3PB [10]. A representative example is $BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$, whose combined A-site Ba richness and multi-valent Co/Fe/Zr/Y B-site chemistry allow concurrent H^+, O^{2-} and h^+ migration through the grain interior, delivering markedly higher intermediate-temperature fuel-cell performance than comparable MIEC cathodes [28]. Thus, TIECs leverage the inherent compositional adaptability of the perovskite lattice more fully than conventional MIECs to support co-migration of multiple charge carriers in the bulk.

A key enabler of TIEC functionality is their defect chemistry, which governs the transport properties of protons, oxygen ions, and electrons. For instance, doping $BaZrO_3$ with Y^{3+} introduces oxygen vacancies that enhance proton transport via hydration reactions [29]. Similarly, the incorporation of Nb^{5+} or Ta^{5+} into layered perovskites stabilises their cubic phase, improving ionic mobility and phase stability under operational conditions [30, 31]. Han and co-workers demonstrated

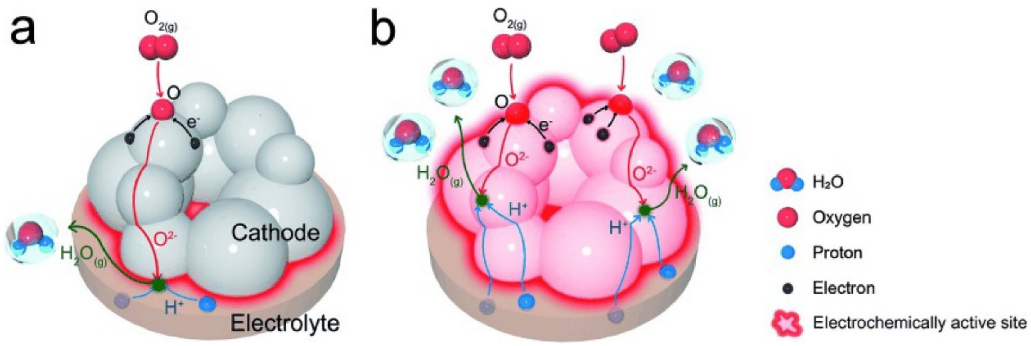


Figure 1. Schematic representation of the ionic conduction mechanism at the H^+-SOFC cathode, showcasing (a) mixed ionic and electronic conductors (O^{2-}/e^-), and (b) a triple-conducting oxide ($H^+/O^{2-}/e^-$). Unlike MIEC materials, which confine electrochemical activity to those at the interface between the proton-conducting electrolyte and the cathode, triple-conducting oxides ($H^+/O^{2-}/e^-$) enable extended charge transport across the entire cathode surface, enhancing reaction zone utilisation and performance. [19] John Wiley & Sons. © 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

improved phase stability for the $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ (BZY20) composition [31].

The versatility of TIECs extends beyond fuel cells to include applications in catalytic membrane reactors and electrolysers [32–34] (figure 2). TIECs have shown promise in enabling innovative processes such as syngas reforming and ethylene production [33]. Similarly, in electrolysers, the simultaneous proton, oxide-ion and electronic conductivity of TIECs allows the water-splitting reaction to proceed throughout the electrode volume, reducing polarisation losses and enabling high hydrogen-production current densities at 400 °C–600 °C, as demonstrated for $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}/BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$ cells operated in electrolysis mode [12].

Despite these advantages, the widespread adoption of TIECs is not without challenges. Material degradation under humid and high-temperature conditions remains a significant barrier to their long-term stability [35–37]. Phase transitions, particularly in perovskite structures, can lead to reduced conductivity and structural instability. These phase changes can be triggered when dopant levels exceed their solubility limit or during high-temperature (800 °C–900 °C) redox cycling in reducing atmospheres, conditions that destabilise the perovskite lattice and sharply lower conductivity [38]. Additionally, the scalability of TIEC synthesis processes must be addressed to enable their integration into commercial devices [39]. Researchers have proposed various strategies to mitigate these issues, including co-doping with high-valence cations, developing composite materials, and leveraging computational modelling to predict and design stable structures [40].

As the energy landscape evolves, the demand for high-performance, sustainable materials will only grow. TIECs, with their unparalleled combination of ionic and electronic conductivity, represent a critical step forward in meeting this demand. By overcoming the limitations of traditional MIECs, they provide a robust platform for the development of next-generation electrochemical devices capable of addressing the dual imperatives of efficiency and sustainability [10].

This review seeks to provide a concise understanding of TIECs, discussing their structure, conduction mechanisms, and applications. The subsequent sections will delve deeper into the case for TIECs as next-generation materials, examining their unique properties and potential in energy conversion and beyond. By highlighting both their achievements and challenges, this review aims to serve as a guide for young researchers, in particular, offering insights into the future trajectory of this promising field.

2. The case for triple ionic–electronic conducting materials

TIECs represent a sizable advancement in the field of materials science, offering distinct advantages over conventional materials used in electrochemical devices [6, 34]. These advantages stem from the simultaneous transport of electrons, protons, and oxygen ions within a single-phase material, a capability that overcomes the limitations of MIECs. By facilitating multi-species conduction, TIECs eliminate the reliance on interfacial DPB and TPBs, which are essential in traditional materials, thereby unlocking superior performance across a wide range of applications [16–18].

The ability of TIECs to extend electrochemical activity beyond the DPBs and TPBs (table 1; it summarises the generic elementary steps governing H^+-SOFC/PCFC cathodes, contrasting MIEC and TIEC behaviour) to the bulk of the material is a defining feature that distinguishes them from other materials [41]. Traditional MIECs rely on the coexistence of ionic and electronic pathways at specific interfacial regions, limiting the scale of reaction zones [17]. In contrast, TIECs enable bulk electrochemical reactions, significantly enhancing reaction kinetics. For instance, $BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$ (BCFZY) has demonstrated exceptional performance as a cathode material for intermediate-temperature SOFC (IT-SOFCs) due to its intrinsic triple-conducting properties, which allow for simultaneous transport of charge carriers throughout the material's bulk [28, 42].

Table 1. The suggested elementary reaction steps for MIEC and TIEC materials-based cathodes. [19] John Wiley & Sons. © 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Reaction step	MIEC materials—Elementary reactions	Reaction step	TIEC materials—Elementary reactions
1	$O_2(g) \longrightarrow 2O_{ad}$	1`	$O_2(g) \longrightarrow 2O_{ad}$
2	$O_{ad} + 2e^-_{cathode} \longrightarrow O^{2-}_{cathode}$	2`	$O_{ad} + 2e^-_{cathode} \longrightarrow O^{2-}_{cathode}$
3	$O^{2-}_{cathode} \longrightarrow O^{2-}_{interface}$	3`	$OH_{Oelectrolyte} \longrightarrow OH^{\cdot}_{Ocathode}$
4	$OH^{\cdot}_{Oelectrolyte} \longrightarrow H^{+}_{interface} + O^{X}_{O}$	4`	$OH^{\cdot}_{Ocathode} \longrightarrow H^{+}_{cathode} + O^{X}_{O}$
5	$H^{+}_{interface} + \longrightarrow O^{2-}_{interface}\ OH^{-}_{interface}$	5`	$2\,H^{+}_{cathode} + \longrightarrow O^{2-}_{cathode}\ H_2O_{cathode}$
6	$H^{+}_{interface} + \longrightarrow OH^{-}_{interface}\ H_2O_{interface}$	6`	$H_2O_{cathode} \longrightarrow H_2O(g)$
7	$H_2O_{interface} \longrightarrow H_2O(g)$		

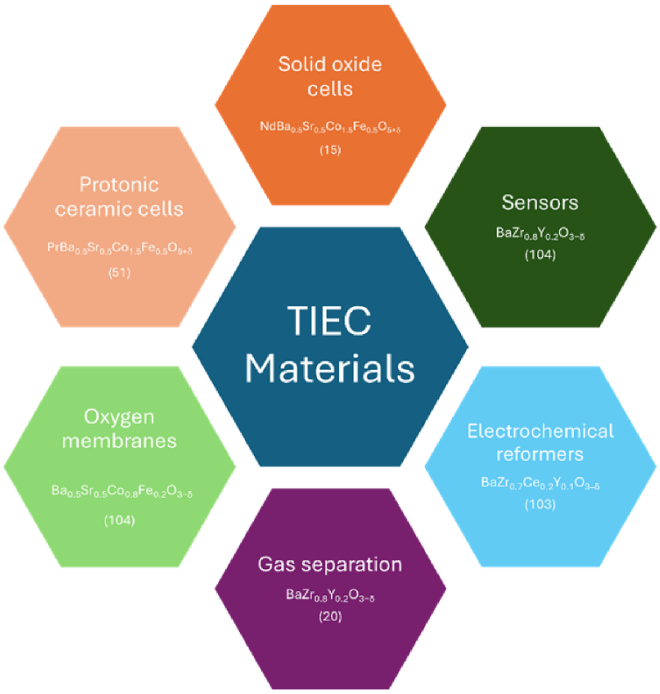


Figure 2. Schematic illustrating versatility of potential applications of TIEC materials.

In addition to expanding reaction zones, TIECs also exhibit superior ORR activity compared to conventional materials [8, 43]. As noted earlier, a $BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$ cathode enhances IT-SOFC performance; even where proton transport is non-essential, its presence facilitates oxygen-vacancy mobility, reinforcing lattice oxygen exchange and thereby strengthening ORR activity [13]. The mixed conduction of oxygen ions and protons in TIECs contributes to more efficient catalytic processes, particularly in SOFCs and PCFCs [34]. Layered perovskites, such as $PrBaCo_2O_{5+\delta}$, have been shown to achieve higher ORR rates due to their ability to facilitate oxygen ion and electron transport along anisotropic diffusion pathways [44].

A critical advantage of TIECs lies in their ability to perform efficiently at intermediate temperatures (400 °C–700 °C). The high-temperature operation, common in traditional SOFCs, often leads to issues such as material degradation, sealing problems, and thermal expansion mismatches [10, 34]. In addition, sustained high-temperature operation can induce chemically driven lattice expansion and oxygen partial pressure–induced stress, promoting interfacial crack initiation, growth, and eventual oxygen electrode/electrolyte delamination [45, 46]. TIECs mitigate these challenges by maintaining high ionic and electronic conductivity at lower operating temperatures. For example, Ba(Zr, Ce)O_3-based perovskites, doped with Y^{3+} exhibit remarkable proton conductivity and structural stability under intermediate-temperature conditions [47]. These materials are particularly well-suited for PCFCs, where their high hydration capacity enhances proton transport while reducing energy losses [48].

The intermediate-temperature operation of TIECs also reduces the thermal stress on device components, improving their durability and lifespan. The Grotthuss mechanism, which facilitates proton transport, is particularly beneficial in maintaining conductivity at lower temperatures, thus contributing to the overall stability and durability of the device [7, 10, 49]. This characteristic is particularly advantageous for applications such as oxygen separation membranes and catalytic membrane reactors, where prolonged exposure to high temperatures can compromise material integrity.

Unlike traditional materials that are limited to single-species conduction, TIECs enable the concurrent transport of multiple charge carriers. This versatility opens new possibilities for device design and functionality. For example, materials like BZY20 exhibit high proton conductivity while maintaining sufficient electronic and oxygen ion conductivity, making them ideal candidates for fuel cells and hydrogen production systems [50–52]. Moreover, the decoupling of oxygen ion and proton transport pathways in TIECs allows for independent optimisation of these properties, a feature that is difficult to achieve in conventional materials [53–56]. In catalytic membrane reactors, this capability supports simultaneous oxygen separation and chemical reactions, enabling processes such as methane reforming and syngas production with higher efficiency than traditional catalysts [10, 19, 57].

TIEC materials can be categorised into key structural families that offer distinct advantages for specific applications. Perovskite-structured oxides (ABO_3 type), such as $BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$, are widely used due to their chemical tunability and ability to accommodate

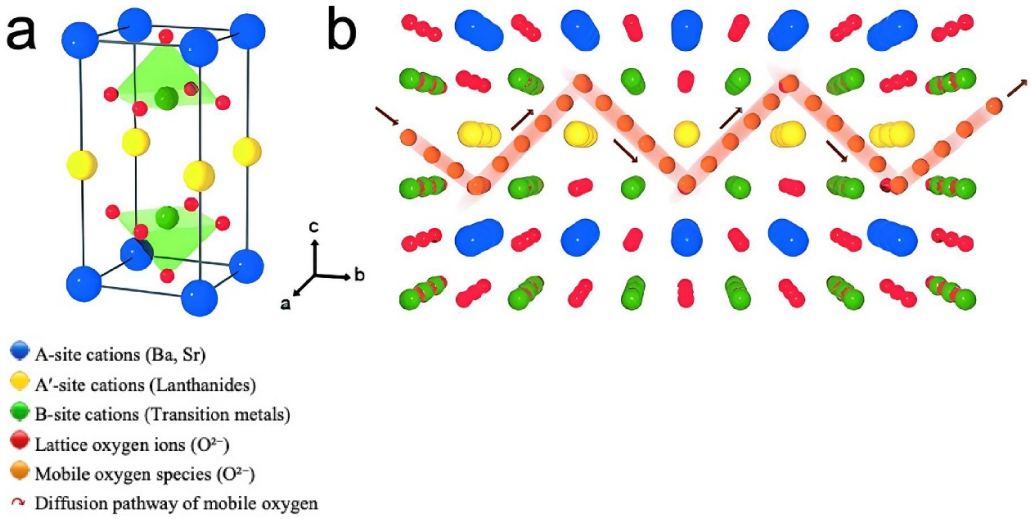


Figure 3. Illustration of (a) the layered perovskite unit cell structure ($AA'B_2O_{5+\delta}$) and (b) a proposed mechanism by Kim and co-workers for bulk diffusion of mobile oxygen species through the pore channels. The blue, yellow, green, red, and orange circles represent A (Ba, Sr), A′ (lanthanides), B (transition metals), O (lattice oxygen), and O (mobile oxygen species), respectively. The layered structure provides pore channels for ion motion in the [Ln–O] and [Co–O] planes that could provide fast paths for oxygen transport. The idea is that the oxygen ion diffusion paths follow a zig–zag-type trajectory through the Co–O plane perpendicular to the Ln–O plane. [19] John Wiley & Sons. © 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

aliovalent dopants, enabling high oxygen-ion and proton conductivities and exceptional cathode performance at intermediate temperatures. Layered perovskite derivatives, particularly Ruddlesden–Popper phases (e.g. $NdBaCo_2O_{5+\delta}$), possess anisotropic diffusion pathways that promote rapid oxygen-ion mobility along specific crystallographic planes, which is advantageous for enhancing surface exchange and reaction kinetics. Other complex oxides, such as double-layered cuprates and emerging high-entropy oxide compositions, are gaining attention for their unique electronic-ionic transport interplay and structural adaptability. Key structural descriptors—such as lattice parameters, ionic radii, and tolerance factors—play a central role in governing charge transport. For instance, $BaCeO_3$ exhibits higher proton conductivity than $BaZrO_3$ due to its larger lattice free volume, which facilitates proton hopping and lowers activation barriers. This classification, when integrated with property comparisons such as charge carrier mobility and defect formation energetics, provides a clearer framework for selecting TIEC materials tailored to application-specific demands across electrochemical devices.

The perovskite structure, with its ABO_3 framework, allows for extensive chemical substitutions at both the A-site and B-site, enabling precise control over defect chemistry and conduction pathways. Zhou and co-workers demonstrated the impact of Ca substitution at the Nd site of $BaNdInO_4$, increasing its total conductivity by 1–2 orders of magnitude [58]. For instance, substituting Ba at the A-site with Sr or La has been shown to enhance oxygen ion conductivity, while B-site substitutions of transition metals like Co or Fe improve electronic conductivity [59]. Lobera *et al,* showed that B-site doping in perovskite-type membranes can significantly enhance oxygen permeability due to the increased electronic conductivity associated with this substitution [60].

Layered perovskites, such as $NdBaCo_2O_{5+\delta}$, offer additional advantages through their anisotropic diffusion pathways [61]. These materials exhibit high oxygen ion mobility along specific crystallographic planes, as validated by computational modelling and experimental studies (figure 3). This anisotropy not only enhances ionic conductivity but also reduces activation energy for oxygen transport, making them highly efficient cathode materials for SOFCs [62, 63].

Traditional electrochemical devices often rely on noble metal catalysts to enhance reaction kinetics, particularly for the ORR and hydrogen oxidation reaction. TIECs, with their intrinsic catalytic activity, reduce the need for expensive noble metals, thereby lowering the overall cost of device fabrication [64]. For example, cobalt-free perovskites like $Ba_{0.95}La_{0.05}Fe_{0.8}Zn_{0.2}O_{3-\delta}$ have demonstrated excellent catalytic performance without requiring noble metal additives, making them cost-effective alternatives for fuel cell cathodes [65].

The chemical and thermal stability of TIECs under operational conditions is a critical advantage for their use in practical applications [66]. For instance, $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ (BCY) and its derivatives exhibit excellent resistance to CO_2 and H_2O, two common sources of degradation in fuel cell environments [10]. This stability ensures consistent performance over extended operational lifetimes, a crucial factor for commercial viability. In addition to their chemical stability, TIECs also exhibit low thermal expansion coefficients, which reduce mechanical stresses during thermal cycling [34]. A representative value for the linear TEC of BZY20 is $10.1 \times 10^{-6}\ K^{-1}$, a comparatively low TEC that supports good thermo-mechanical compatibility

with typical electrolytes and helps mitigate thermally induced stresses during cycling [67, 68]. This property is particularly beneficial for applications such as oxygen separation membranes and high-temperature electrolysis, where materials are subjected to repeated heating and cooling cycles.

While much of the focus on TIECs has been on their application in fuel cells, their versatility extends to other electrochemical systems [69]. In catalytic membrane reactors, TIECs enable the simultaneous conduction of protons, oxygen ions, and electrons, facilitating complex chemical reactions such as ammonia synthesis and hydrocarbon reforming [10, 70]. Their ability to operate under harsh chemical environments and at intermediate temperatures makes them ideal for these applications. Ma *et al* recently reported a highly efficient triple-conducting perovskite material, $Ba_{0.95}Fe_{0.7}Co_{0.2}Sc_{0.1}O_{3-\delta}$ (BFCS0.95), for low-temperature SOFCs [71]. Furthermore, the potential for TIECs to be used as mixed-conducting membranes in CO_2 separation and hydrogen production systems further broadens their applicability [70]. By combining high ionic conductivity with robust chemical stability, TIECs have the potential to offer a unique platform for advancing sustainable energy technologies.

However, the extent to which these materials exhibit true triple conductivity has been a subject of scientific scrutiny. One challenge in confirming triple conductivity arises from the complex defect chemistry and transport mechanisms within these materials. The simultaneous conduction of multiple charge carriers can lead to intricate interactions, making it difficult to isolate and measure each carrier's contribution accurately. For instance, the presence of mobile protons, oxygen vacancies, and electronic holes necessitates a comprehensive understanding of defect formation and conduction pathways, which are not yet fully elucidated [72]. Moreover, the proton conduction in many perovskite oxides is often limited due to insufficient hydration levels. Achieving significant proton conductivity requires materials to incorporate adequate water content, which is not always feasible under typical operating conditions. This limitation raises questions about the practical proton conductivity in these materials [73]. This criticism is especially relevant in their proclaimed applications in SOFCs since these devices only require oxide ion and electronic conductivity.

Nevertheless, as the global energy landscape shifts towards renewable and sustainable energy sources, the demand for high-performance materials that can efficiently convert and store energy is growing. TIECs, with their unparalleled combination of ionic and electronic conductivity, are poised to play an important role in this transition [10].

3. Conduction mechanisms in triple ionic–electronic conductors

The promising functionality of TIECs arises from their ability to facilitate the simultaneous transport of electrons, oxygen ions, and protons. This section provides a detailed discussion of the mechanisms (table 2) underlying these transport processes, integrating experimental and theoretical insights to offer a comprehensive understanding of their conduction pathways.

3.1. Proton conduction mechanisms

Proton conduction in TIECs primarily occurs through the Grotthuss mechanism, which involves the hopping of protons between adjacent lattice oxygen atoms [74] (figure 4). This process is facilitated by hydration reactions, where water molecules dissociate, and protons are incorporated into the lattice [75, 76]. Materials such as $BaZrO_3$ and $BaCeO_3$ exhibit high proton conductivity due to their ability to incorporate significant amounts of water at elevated temperatures [77, 78].

Experimental studies on BZY20 highlight its exceptional proton conductivity, attributed to the formation of strong hydrogen bonds and large free volumes within the lattice [51, 52]. Impedance spectroscopy measurements on BZY20 demonstrate a significant reduction in activation energy for proton transport compared to undoped $BaZrO_3$ [51]. Theoretical models have extensively studied proton conduction, with a focus on the Grotthuss mechanism. In $BaZrO_3$-based systems, density functional theory (DFT) simulations reveal that proton transport is heavily influenced by local lattice distortions around oxygen vacancies [79]. The introduction of dopants such as Y^{3+} creates an energetically favourable environment for proton hopping. Studies on BZY20 indicate that Y^{3+} doping reduces the energy barrier for proton migration to as low as 0.35 eV, making it highly efficient for intermediate-temperature applications [52, 80].

In $BaCeO_3$ systems, theoretical models have shown that the larger lattice volume compared to $BaZrO_3$ enhances proton mobility by reducing the proton hop distance [81]. Cerates on their own, however, suffer from low thermal and chemical stability and zirconates, too, on their own, suffer from low proton conductivities. It is, therefore, the mixed compositions of cerates and zirconates such as $BaZr_{1-x}Ce_xY_{0.2}O_{3-\delta}$ and $BaZr_{0.1}Ce_{0.7}Y_{0.2-x}Yb_xO_{3-\delta}$ that are currently state-of-the-art materials for high-temperature proton conducting devices [82, 83].

Recent studies suggest that co-doping with high-valence elements such as Nb^{5+} can stabilise the lattice without significantly compromising proton mobility [84]. In this regard, layered perovskites, such as $NdBaCo_2O_{5+\delta}$, have been investigated and shown to exhibit proton conduction, though their mechanisms differ due to the anisotropic nature of their crystal structure [85]. These materials leverage unique diffusion pathways along specific crystallographic planes, as validated through neutron diffraction studies [86]. Computational simulations have shown that the arrangement of oxygen sites in layered structures facilitates proton hopping with minimal energy barriers, providing an alternative to conventional perovskite mechanisms [87, 88].

3.2. Oxygen ion transport mechanisms

Oxygen ion conduction in TIECs is governed by the migration of oxygen vacancies within the crystal lattice. These vacancies are introduced through aliovalent doping, which replaces

Table 2. Summary of conduction mechanisms in triple-ionic–electronic conducting oxides.

Carrier/process	Mechanistic basis	Dominant mobile defects/ species	Representative materials
Proton conduction (Grotthuss hopping)	Successive proton transfer between adjacent lattice O (rotation + hopping sequence)	Protonic defects via hydration/hydrogenation (OH_O$^{\bullet}$)	BZY20; $BaCeO_3$; $BaZr_{1-x}Ce_xY_{0.2}O_{3-\delta}$; $BaZr_{0.1}Ce_{0.7}Y_{0.2-x}Yb_xO_{3-\delta}$; $NdBaCo_2O_{5+\delta}$
Oxygen ion conduction (vacancy diffusion)	Hopping of O^{2-} through oxygen vacancies	Vacancies from aliovalent doping (e.g. Y^{3+}, mixed B-site)	BCFZY; $GdBaCo_2O_{5+\delta}$; $NdBaCo_2O_{5+\delta}$
Electronic conduction (small-polaron hopping)	Thermally activated hole hopping on TM sites via B–O–B network	Localised holes on Co^{3+}/Co^{4+}, Fe	BCFZY; $PrBaCo_2O_{5+\delta}$; $NdBaCo_2O_{5+\delta}$; $BaCoO_3$ variants
Coupled transport (proton-vacancy-hole)	Mutual modulation: vacancies enable hydration; protons aid vacancy mobility; vacancy fields aid polaron hopping	Coexisting H^+, V_O$^{\bullet\bullet}$, h$^{\bullet}$	Y-doped $BaZrO_3$; $BaZr_{0.8}Ce_{0.2}O_{3-\delta}$; $NdBaCo_2O_{5+\delta}$

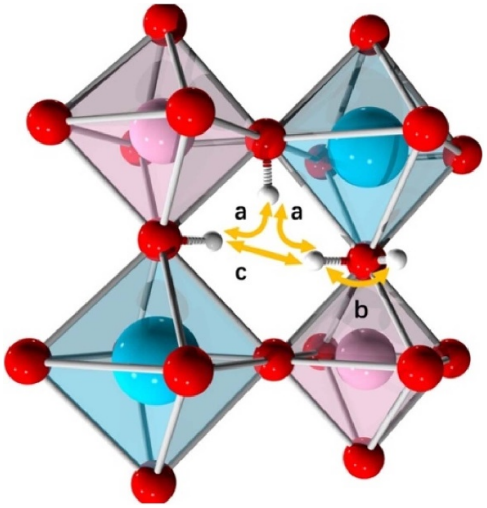


Figure 4. Proton migration in the perovskite structure based materials (a) intraoctahedral hopping (b) reorientation and (c) intraoctahedral hopping. Reprinted with permission from [74]. Copyright (2014) American Chemical Society.

host ions with cations of a different valence. For example, doping $BaZrO_3$ with trivalent cations such as Y^{3+} or Sc^{3+} creates oxygen vacancies that act as diffusion sites for oxygen ions [89, 90].

Experimental studies on $BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$ (BCFZY) have demonstrated high oxygen ion conductivity, making it a promising material for IT-SOFCs [91, 92]. Electrical conductivity relaxation experiments have shown that the diffusion coefficient for oxygen ions in BCFZY is significantly enhanced under humid conditions, where additional proton transport pathways are activated [93]. This dual-mode conduction makes BCFZY particularly effective for applications requiring simultaneous oxygen and proton conduction.

In layered perovskites, oxygen ion transport benefits from their unique structural features. Studies on $GdBaCo_2O_{5+\delta}$ using advanced characterisation methods such as isotope exchange depth profiling, reveal that oxygen diffusion predominantly occurs along the Co–O planes [94]. These diffusion pathways are highly anisotropic, resulting in enhanced ionic mobility along specific directions while maintaining structural stability [85, 86]. Molecular dynamics (MD) simulations complement these findings by mapping oxygen ion diffusion pathways in both perovskite and layered oxide systems. Similarly, for $NdBaCo_2O_{5+\delta}$, MD models predict anisotropic diffusion along the Co–O planes, with low activation energies [23]. This theoretical insight aligns with experimental observations of high oxygen ion mobility, validating the role of structural anisotropy in enabling efficient transport.

3.3. *Electronic conduction mechanisms*

Electronic conduction in TIECs is typically mediated by small-polaron hopping, a process where charge carriers (electrons or holes) localise on specific sites and hop between neighbouring sites [47]. This mechanism is particularly relevant in transition metal-based perovskites, where the oxidation states of B-site cations fluctuate during conduction [43]. For instance, cobalt-based perovskites, such as $BaCoO_3$, exhibit high electronic conductivity due to the ease with which $Co^{3+/}Co^{4+}$ redox couples facilitate small-polaron hopping [95, 96].

In layered perovskites like $PrBaCo_2O_{5+\delta}$, the electronic conductivity benefits from the arrangement of B-site cations, which promotes extended electronic states along the Co–O planes [97, 98]. For $PrBaCo_2O_{5+\delta}$, this is confirmed by computational studies that show that the layered structure facilitates electronic conduction by enabling extended Co–O–Co networks [99]. This connectivity reduces the energy barrier for electron hopping, particularly in the Co^{3+}/Co^{4+} redox system. Theoretical models also highlight the importance of cation ordering in reducing polaron localisation, further improving electronic mobility. Neutron diffraction studies confirm that the layered structure enables efficient charge transfer, while computational models highlight the role of cation ordering in reducing the activation energy for electron transport [99, 100].

3.4. Defect chemistry and coupled transport phenomena

One of the defining features of TIECs is their ability to support coupled transport phenomena, where the movement of one charge carrier influences the behaviour of others. This coupling is particularly evident in materials like $BaZrO_3$-based perovskites, where proton and electron transport are interdependent [101, 102]. Defect chemistry plays a central role in coupled transport phenomena. Theoretical studies on $BaZrO_3$ doped with Y^{3+} reveal that the presence of oxygen vacancies enhances proton incorporation through hydration reactions [89]. These vacancies act as stabilisation sites for protons, reducing the energy barrier for proton hopping and promoting coupled oxygen ion and proton transport [101].

Experimental studies on $BaZr_{0.8}Ce_{0.2}O_{3-\delta}$ reveal that the introduction of oxygen vacancies not only enhances oxygen ion transport but also facilitates proton incorporation [103]. This coupling is supported by first principle calculations, which show a proportional increase in proton and oxygen ion conductivity under humid conditions [104]. Layered perovskites also exhibit strong coupling effects. For example, $NdBaCo_2O_{5+\delta}$ demonstrates a unique interplay between oxygen ions and electron transport, where the movement of oxygen ions along specific planes promotes electron mobility through adjacent transition metal sites [105, 106]. MD simulations show that the movement of oxygen vacancies creates localised electric fields, facilitating small-polaron hopping in adjacent Co–O planes [23]. This coupling is critical for achieving high performance in fuel cell applications. This coupling is particularly advantageous in fuel cells, where the simultaneous transport of multiple species is essential for efficient operation.

Beyond the foundational mechanisms of ionic and electronic conduction in TIECs, significant advances have been made in enhancing transport through chemical and structural design. Aliovalent doping is a widely used strategy to tailor defect populations and mobility. For example, in $BaZrO_3$, Y^{3+} doping introduces oxygen vacancies and lowers the activation energy for proton migration to $\sim$0.35 eV, substantially improving protonic conductivity. Recent research has explored doping gradients to spatially modulate defect concentrations, especially at interfaces where conductivity is most critical, although empirical optimisation remains ongoing. Strain engineering has also emerged as a promising technique: interfacial or epitaxial strain can modify local lattice geometry, thereby lowering migration energy barriers and enhancing oxygen-ion mobility by altering defect formation energetics. Lattice-mismatched heterostructures have demonstrated order-of-magnitude increases in ionic conductivity under tensile strain. Additionally, interface nanostructuring, particularly in mixed-phase or composite systems, enables synergistic transport enhancement. Nanostructured heterojunctions between perovskite phases can generate built-in electric fields that facilitate defect migration, while nanoscale dispersion in composite electrodes extends percolation networks for both ionic and electronic carriers. These strategies, grounded in fundamental principles of defect chemistry, migration energetics, and interfacial physics, provide critical tools for improving electrochemical performance in next-generation TIEC-based devices.

4. Applications of triple ionic–electronic conductors

SOFCs are one of the most prominent applications of TIECs, benefiting significantly from their unique triple-conducting properties. TIECs, by enabling bulk conduction, expand the reaction zone across the entire material, significantly enhancing performance. For example, $BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$ (BCFZY) has shown exceptional performance as a cathode material for IT-SOFCs [28, 42]. Studies demonstrated that BCFZY exhibits high oxygen ion conductivity due to its extensive oxygen vacancy network, while its proton conduction capability enhances reaction kinetics under humidified conditions. Recently Ma and co-workers demonstrated an A-site-deficient and triple-conducting $Ba_{0.95}Fe_{0.7}Co_{0.2}Sc_{0.1}O_{3-\delta}$ perovskite composition for more efficient and durable oxygen reduction electrocatalysis in LT-SOFCs [71]. Xia *et al* demonstrated that the triple-conducting perovskite $BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$ serves as an effective electrolyte, facilitating ionic transport through a built-in electric field created by a heterojunction effect, which enhances the overall electrochemical performance of the fuel cell [42].

Furthermore, the integration of TIECs into battery systems has been explored, with promising results. For example, Wang *et al* reported on the development of ion/electron co-conductive interfaces that facilitate rapid redox reactions in lithium-sulphur batteries, showcasing how TIECs can enhance battery performance by improving charge transfer kinetics [107]. This aligns with the observations of Casado *et al* who noted that mixed conductors with high ionic and electronic conductivities are essential for the efficiency of membrane electrode assemblies in electrochemical devices, including batteries and fuel cells [108]. The ability of TIECs to operate effectively in both fuel cells and batteries illustrates their multifunctional capabilities, which are crucial for advancing energy storage technologies.

PCFCs (figure 5) operate at intermediate temperatures (400 °C–700 °C), a range where proton conduction dominates. TIECs are well-suited for their applications, and recently, material compositions such as BZY20 have been extensively studied for PCFC applications [31]. Additionally, BCY and its derivatives have been employed in PCFCs for their dual benefits of high proton transport and chemical stability. Experimental studies have shown that these materials are resistant to CO_2 and H_2O poisoning, two common challenges in fuel cell environments [10]. Their high hydration capacity and compatibility with TIEC cathodes further enhance the overall efficiency and durability of PCFC systems. Material compositions such as BCFZY0.1 have been shown to have promising potential as cathodes in PCFCs due to their TIEC nature [7, 34]. Gong *et al* demonstrated an excellent peak power density of 0.84 W cm^{-2} at 550 °C and durability for the multicomponent Co-free

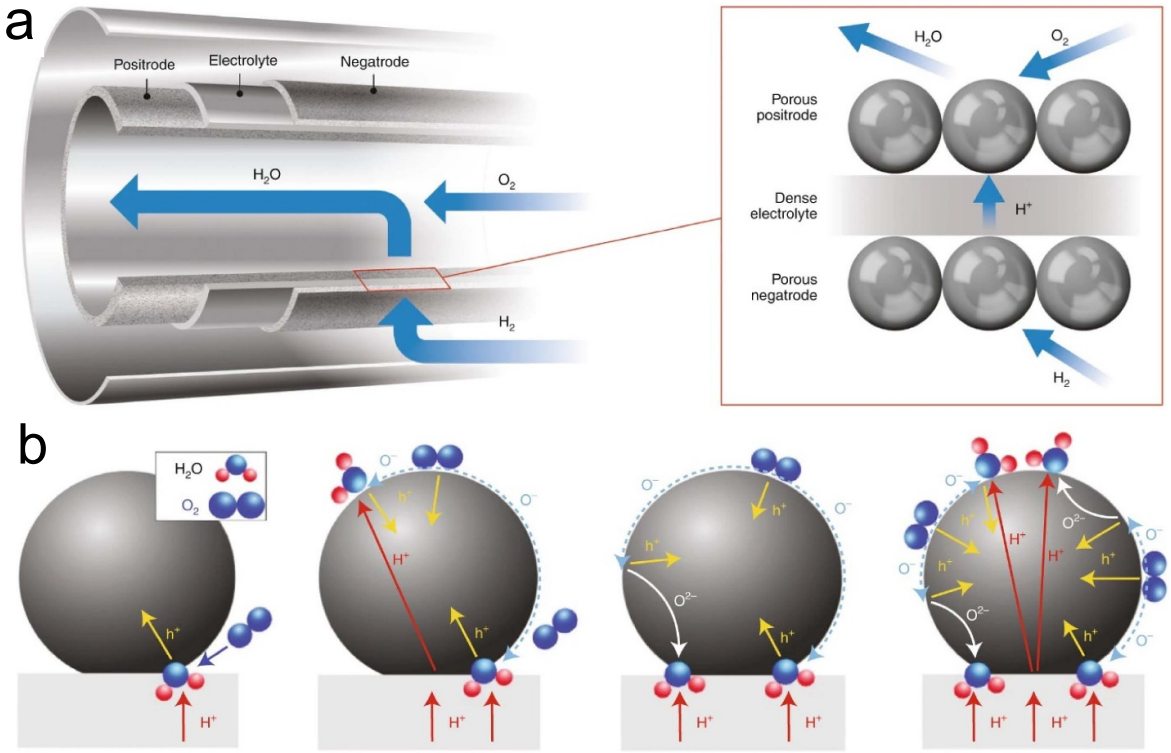


Figure 5. Schematic illustration of a protonic ceramic fuel cell (PCFC). The device comprises a three-layer structure consisting of a porous positrode, a dense electrolyte, and a porous negatrode. Hydrogen is oxidised at the negatrode, generating protons that are transported through the electrolyte to the positrode. At the positrode, oxygen is reduced and reacts with the transported protons to form water. The inset highlights the direction of reactant and product flow at each interface. This configuration is reversible and can also operate as an electrolysis cell under appropriate conditions. (b) Schematic comparison of bulk and surface transport pathways and positrode reaction sites within a single particle for four material types: (from left to right) a pure electronic conductor, an H^+/h^+ mixed ionic–electronic conductor (MIEC), an O^{2-}/h^+ MIEC, and a triple ionic–electronic conductor (TIEC) conducting H^+, O^{2-}, and h^+. The number and spatial distribution of electrochemically active sites increase with the number of mobile charge carriers, with TIEC materials enabling the most extensive reaction zones. Reaction sites are represented by the presence of H_2O on the particle surface. Reproduced from [10], with permission from Springer Nature.

$Pr_3Ni_{1.5}Cu_{0.3}Nb_{0.05}Ta_{0.05}Zr_{0.05}Y_{0.05}O_{7-\delta}$ (PNCNTZY) triple conducting PCFC cathode (figure 6) [109].

The role of TIECs in hydrogen production through water splitting has gained significant attention in recent years. Proton-conducting oxides such as BZY20 have been integrated into protonic ceramic electrolysers, achieving high efficiency and durability [110]. These materials enable effective proton transport while maintaining chemical stability under humidified conditions, essential for water electrolysis. Vollestad and co-workers recently showed an efficient novel protonic ceramic electrolyser cell (PCEC) anode $Ba_{1-x}Gd_{0.8}La_{0.2+x}Co_2O_{6-\delta}$ which exhibits mixed p-type electronic and protonic conduction and has demonstrated low activation energy for water splitting [111]. Duan *et al* demonstrated the reversible PCECs for energy conversion and versatile production and conversion of H_2, syngas and hydrocarbons with high round-trip efficiency (75%) and long-term stable operation. In addition, solid-state $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ TIECs have been demonstrated as efficient catalytic membrane reactors for syngas production via methane reforming [112].

The ability of TIECs to conduct oxygen ions efficiently has made them strong candidates for oxygen separation membranes [113]. These membranes are critical for processes such as oxy-fuel combustion and gas purification, where the selective transport of oxygen is required. Perovskite-based TIECs like $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) have demonstrated high oxygen flux rates, making them ideal for these applications [114]. Studies using oxygen permeation measurements have shown that BSCF membranes can achieve high separation efficiencies at intermediate temperatures, reducing energy consumption compared to traditional systems [115].

5. Challenges and future directions

TIECs have demonstrated vast potential for electrochemical devices through their unique ability to transport multiple charge carriers. However, despite their advantages, significant challenges remain in their material design, scalability, and operational stability. Also, given the potential of applications of these materials in several technologies, the challenges are

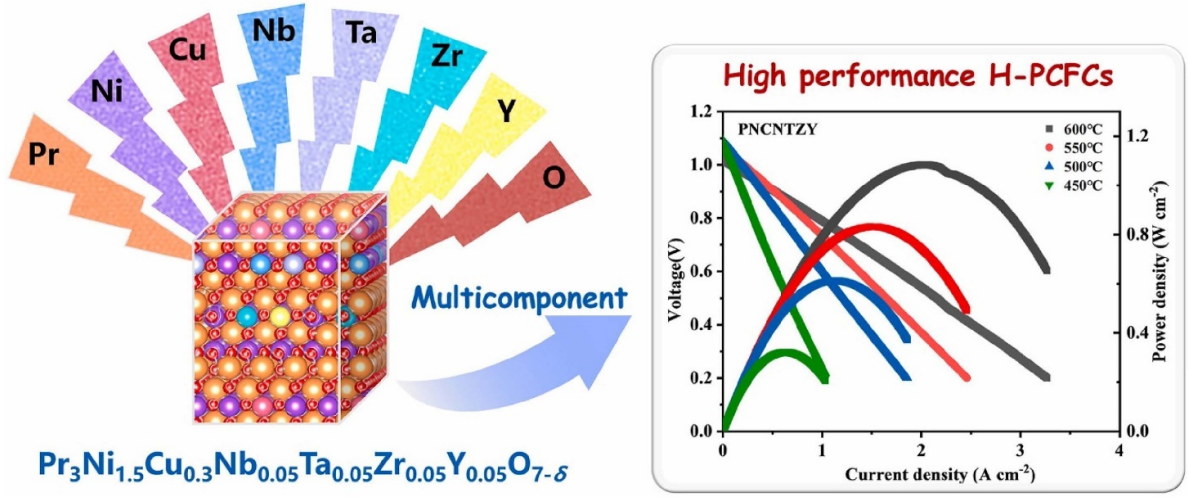


Figure 6. A multicomponent Co-free triple conducting SOFC cathode showing promising power density. Reprinted from [109], Copyright (2024), with permission from Elsevier.

varied. For example, while PCFCs and PCECs share a similar materials framework, PCECs face more extreme conditions such as higher voltages, and severe degradation in oxygen evolution, making electrode stability a more pressing issue [116]. Meanwhile, in PCFCs, hydrocarbon fuel tolerance and redox stability of the anode remain key challenges [117]. Nevertheless, this section discusses the general challenges and proposes pathways to address them, ensuring the realisation of TIECs' full potential.

5.1. Material stability and long-term durability

One of the most critical challenges facing TIECs is their chemical and structural stability under operating conditions. Materials such as $BaCeO_3$ and $BaZrO_3$, while offering high proton conductivity, are susceptible to degradation in the presence of CO_2, H_2O, or sulphur-containing environments [118]. $BaCeO_3$, for instance, reacts with CO_2 to form barium carbonate, leading to a significant loss in conductivity and structural integrity. Mixed systems of barium cerates and zirconates address the main challenge of stability encountered in cerates and zirconates respectively. The state-of-the-art materials for high-temperature proton conducting materials are essentially the solid solutions of doped barium cerates and zirconates. For example, the composition, $BaZr_{1-x}Ce_xY_{0.2}O_{3-\delta}$ ($0.0 \leqslant x \leqslant 0.8$) (BZCY) has been widely studied particularly for a synergetic combination of stability originating from zirconates and high proton-conduction emanating from the cerates [82, 119]. The mixed materials are stable in both H_2O and CO_2 atmospheres. Co-doping strategies have particularly proved useful [22, 23]. Similarly, the incorporation of dopants such as Y^{3+} has been shown to enhance the chemical resilience of $BaCeO_3$ while maintaining its high conductivity [29]. Future research should focus on optimising dopant concentrations and exploring new combinations of dopants to balance conductivity and stability.

Layered perovskites like $NdBaCo_2O_{5+\delta}$ also face stability issues, particularly under high-temperature and oxidative conditions [30, 31]. Oxygen vacancy ordering in these materials can lead to phase transitions that compromise their ionic and electronic transport properties. Theoretical and experimental studies suggest that tailoring the A-site cation composition can reduce phase instability. For example, the incorporation of different cations at the A-site has been demonstrated to enhance the chemical stability and electrical conductivity of layered perovskites like $LaBaCo_2O_{5+\delta}$ [120]. This approach is supported by findings that indicate the stabilization of oxide ion vacancies through careful selection of A-site cations, which can lead to improved performance in high-temperature applications [121, 122]. Moreover, the ability to tailor the A-site cation composition has been linked to the optimisation of oxygen stoichiometry, further contributing to the stability of these materials under varying operational conditions [61].

The long-term durability of TIECs under operational conditions is a critical factor for their commercialisation. Prolonged exposure to high temperatures, humid environments, and reactive gases can lead to structural degradation, phase transitions, and performance loss. For example, studies on BCFZY have shown that its oxygen vacancy network becomes less active over time, reducing its ionic conductivity [123, 124]. Strategies to enhance durability include surface modifications and protective coatings. Applying thin, chemically inert layers to the surface of TIECs can prevent interactions with harmful gases while maintaining their transport properties [125].

5.2. Scalability and synthesis challenges

The scalability of TIEC production presents another significant barrier to their widespread adoption. Current synthesis methods, such as solid-state reactions, often require high temperatures and prolonged sintering times, making

them energy-intensive and cost-prohibitive for large-scale production [126]. Additionally, these methods frequently result in inhomogeneous microstructures, which can adversely affect transport properties.

To address these challenges, advanced synthesis techniques such as sol–gel processing, co-precipitation, and spray pyrolysis have been explored [127, 128]. These methods offer better control over particle size and distribution, leading to more uniform microstructures. However, their scalability remains limited, and further advancements are needed to develop cost-effective, industrial-scale synthesis processes. Additionally, additive manufacturing techniques, such as 3D printing, have recently gained attention as a potential solution for fabricating complex TIEC structures [129]. By enabling precise control over material composition and geometry, these methods can optimise device performance while reducing material waste. A special focus on adapting these techniques for TIECs, particularly for applications in fuel cells and catalytic membranes could prove useful.

5.3. *Transport property optimisation*

While TIECs exhibit multi-species conduction, achieving an optimal balance between ionic and electronic transport remains challenging. For instance, high proton conductivity in materials like $BaZrO_3$ is often accompanied by reduced electronic conductivity, which can limit their performance in certain applications [130]. Similarly, oxygen ion transport in layered perovskites is highly anisotropic, which can lead to performance inconsistencies in isotropic device architectures [131]. A related optimisation challenge in using these materials is optimising the temperature range since oxide ion transport is typically faster at high temperatures (>500 °C) and proton transport faster at relatively low temperatures (<500 °C).

To address these issues, defect engineering has emerged as a promising approach. By manipulating the type, concentration, and distribution of defects, researchers can tailor the transport properties of TIECs to meet specific application requirements. For example, introducing oxygen vacancies through aliovalent doping has been shown to enhance both proton and oxygen ion conductivity in $BaZrO_3$-based materials [132]. Composite materials also offer a pathway for transport property optimisation. By combining TIECs with other conductive phases, researchers have reported synergies that enhance overall performance. For instance, composites of $BaCeO_3$ and $BaZrO_3$ have demonstrated improved ionic conductivity and chemical stability compared to their individual components [133–135] (figure 7). Mixed doped barium cerate-zirconate perovskites ($BaZr_{1-x}Ce_xY_{0.2}O_{3-\delta}$, $0 \leqslant x \leqslant 0.8$) retain phase integrity and show CO_2/H_2O tolerance superior to pure $BaCeO_3$ while sustaining high proton conductivity, thereby exemplifying simultaneous conductivity and stability optimisation [82, 119]. Y-doped BZY20 likewise exhibits improved phase stability under operating conditions [31, 51].

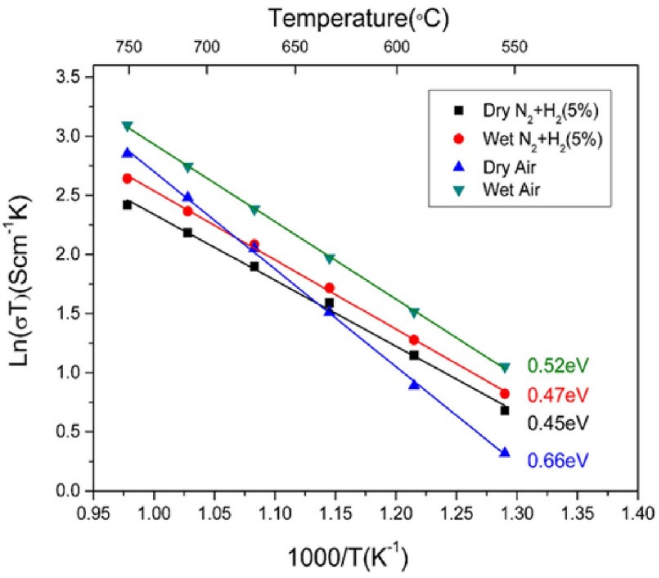


Figure 7. The total conductivity of BZCYYb in different atmospheres demonstrates its superior oxide and protonic conductivity. [135] John Wiley & Sons. © 2019 Curtin University and John Wiley & Sons, Ltd.

5.4. *Computational and data-driven approaches in TIEC design*

Recent advances in computational modelling and data science are transforming the way TIECs are discovered and optimised. By offering atomistic insight into transport behaviour and enabling large-scale screening of potential candidates, these approaches complement experimental efforts and significantly reduce the time and resources required for materials development. Techniques such as MD simulations and DFT-based high-throughput workflows are particularly well suited for probing complex transport mechanisms and assessing compositional stability across diverse chemistries. Moreover, the integration of machine learning (ML) tools with computational databases is helping to guide synthesis by predicting key materials properties. Together, these computational strategies provide a predictive framework that sets the stage for more targeted experimental exploration. The following section outlines specific examples where these tools have been successfully applied to TIEC development, highlighting their growing role in accelerating materials discovery and design.

Advanced computational tools, such as ML and high-throughput screening, can accelerate the discovery of new TIEC compositions. Such methods would enable researchers to predict transport properties, stability, and performance under various conditions, guiding experimental efforts. High-throughput computational screening has emerged as a powerful tool for identifying new candidates for hydrogen evolution electrocatalysts [136, 137]. Screening studies use DFT-based workflows to evaluate thousands of potential compositions for their ionic and electronic transport properties.

Moreover, the application of high-throughput screening techniques has been instrumental in identifying new materials with enhanced properties. For example, the combinatorial synthesis and screening of high-entropy oxide electrocatalysts have demonstrated the effectiveness of high-throughput methods in rapidly identifying active compositions and understanding compositional trends [138]. Such advancements underscore the importance of integrating computational and experimental approaches in the quest for novel TIEC materials. Furthermore, most research has focused on p-type TIECs; the development of n-type variants could expand their applicability in devices operating under reducing conditions. For example, computational studies suggest that doping $BaZrO_3$ with transition metals like Ti or Nb could enhance its n-type conductivity [139].

5.5. Concluding remarks

In conclusion, the exploration of TIEC materials represents a rapidly advancing and strategically important frontier in materials science, with transformative potential for electrochemical energy conversion and storage technologies. These materials, uniquely capable of transporting multiple charge carriers simultaneously, offer integrated functionality that can significantly reduce interfacial resistances and extend electrochemical reaction zones in devices such as SOFCs, electrolyser cells, and permeation membranes.

This review has highlighted how the structural versatility of perovskite-based and layered oxide frameworks enables fine-tuning of defect chemistry, allowing for the optimisation of oxygen-ion, proton, and electronic transport. The incorporation of aliovalent doping strategies, strain modulation, and nanoscale heterostructuring has further expanded the design space, enabling materials with improved performance at intermediate temperatures. Additionally, the emergence of computational and data-driven methods such as molecular dynamics simulations, high-throughput DFT screening, and ML will accelerate the discovery of novel TIEC compositions and provide predictive insight into their behaviour.

By offering a systematic overview of material classes, conduction mechanisms, performance metrics, and future design strategies, this work provides a roadmap for the rational design and application of TIEC materials. The convergence of fundamental understanding and emerging synthesis and characterisation techniques makes this an opportune time to harness the full potential of TIECs in next-generation energy systems. Continued interdisciplinary efforts, spanning experimental, theoretical, and computational domains, will be essential to translate the promise of these materials into scalable, durable, and efficient electrochemical technologies.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Author contributions

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Conceptualization (lead), Data curation (lead), Formal analysis (lead), Methodology (lead), Project administration (lead), Visualization (lead), Writing – original draft (lead), Writing – review & editing (equal)

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