

Ba(Ce,Zr)O₃-based electrodes for protonic ceramic electrochemical cells: towards highly compatible functionality and triple-conducting behaviour

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Protonic ceramic fuel cells and electrolysis cells represent low- and intermediate-temperature electrochemical devices, which allow chemical-to-electrical energy conversion with very high efficiency and low environmental impact. In order to ensure the long-term operability of these devices, as well as to provide for their up-scaling, a number of existing challenges associated with chemical and thermal incompatibilities pertaining to the functional materials remain to be overcome. This work presents a comprehensive overview of new electrode materials based on barium cerate/zirconate. The structural fragments of these materials are similar to those of the proton-conducting Ba(Ce,Zr)O₃ electrolytes, which causes superior chemical compatibility between different functional materials. The primary emphasis of the research is on the functional properties of these materials such as chemical stability, thermal expansion behaviour and transport features. This in turn determines the electrochemical performance of the designed electrodes. In addition, the possibility of obtaining triple-conducting materials is discussed as means of designing electrodes with a high electrochemical active surface area required for the design of high-performance protonic ceramic fuel and electrolysis cells.

The bibliography includes 208 references.

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1. Introduction

Proton-conducting materials based on complex oxides are extensively studied, being of great interest in terms of both fundamental and applied science.^{1–5} At elevated temperatures, such oxide systems, which are naturally free from hydrogen in any form, have the potential to interact with the hydrogen-containing components of a gas atmosphere,

resulting in the production of protons. Due to their beneficial crystallochemical characteristics, some complex oxides allow the formation of a high concentration of protons, which can result in predominantly protonic transportation.⁶ This feature represents applied advantages compared with conventional oxygen-ionic conductors due to the lower potential barrier and higher mobility of protons. As a result, such proton-conducting materials provide a good basis for

the fabrication of various electrochemical cells. Currently, a proton-conducting sign has been revealed for numerous compounds based on such parent phases as $\text{La}(\text{Y}, \text{Yb})\text{O}_3$,^{7,8} LaScO_3 ,⁹ CaZrO_3 ,¹⁰ SrCeO_3 ,¹¹ SrZrO_3 ,¹² $\text{Ba}_2\text{In}_2\text{O}_5$,¹³ $\text{Ba}_2\text{CaNbO}_{5.5}$,¹⁴ LaNbO_4 ,¹⁵ $\text{La}_2\text{Ce}_2\text{O}_7$,¹⁶ $\text{La}_2\text{Zr}_2\text{O}_7$,¹⁷ $\text{La}_6\text{MoO}_{12}$,¹⁸ *etc.* Among them the materials based on BaCeO_3 (cerates) or BaZrO_3 (zirconates) have been broadly studied as one of the most pronounced proton conductors.^{1–6}

From the viewpoint of their potential operation across low- and intermediate-temperature ranges, protonic ceramic fuel cells (PCFCs) and protonic ceramic electrolysis cells (PCECs) compete with cells based on oxygen-conducting electrolytes, *i.e.* solid oxide fuel cells (SOFCs) and solid oxide electrolysis cells (SOECs).^{1–5} Since their mode of energy conversion approaches single-step, resulting in quite high overall efficiency, PCFCs and PCECs are promising electrochemical systems.^{19,20} Due to their high theoretical attractiveness for developing hydrogen and electrochemical energy fields, the problem of obtaining high practical performance and corresponding long-term stability is becoming increasingly urgent as a means of ensuring the future commercialisation of PCFCs/PCECs.

One of the possible approaches for achieving excellent operational conditions in electrochemical systems lies in careful modification of the electrode materials, which must satisfy a number of strict requirements:^{21–24} phase stability, chemical compatibility, suitable thermo- and chemico-mechanical properties, high electronic conductivity, acceptable ionic transportation, high tolerance to poisoning and, finally, excellent electrochemical (electrocatalytic) performance. In this regard, various single-phase oxides, composite materials and heterogeneous systems have been successfully adopted as oxygen or steam electrodes to provide oxygen reduction (ORR) and water evolution (WER) reactions, which determine the overall efficiency and performance of low- and intermediate-temperature PCFCs/PCECs based on thin-film electrolytes.^{25–27} Among existing alternatives, the design of electrodes based on BaCeO_3 , BaZrO_3 or $\text{Ba}(\text{Ce}, \text{Zr})\text{O}_3$ and doped with transition elements is considered as one of the contemporary trends. This is due to a synergetic effect: on the one hand, a basic perovskite structure is maintained to provide possible proton transportation as well as superior chemical and mechanical compatibilities with the corresponding electrolytes; on the other hand, the existence of redox-active elements in large

quantities results in enhanced electrical and electrochemical properties.

Although many review articles have been published in the last few years, they describe different aspects of proton-conducting electrolytes, including proton transportation behaviour,^{1,2} materials design,^{4,6} technological issues^{28,29} or application features.^{3,15,30,31} In this brief review, we highlight the recent achievements in the design and development of PCFCs and PCECs, the functional components of which are based on the same fragmentary type of ABO_3 ($\text{A} = \text{Ba}$, $\text{B} = \text{Ce}$, Zr or Ce/Zr). In particular, the main focus of the present review is directed towards the functional properties of M-doped ABO_3 materials (M is a transition element) which can serve not as electrolytes, but as electrodes of PCFCs and PCECs and their role in the achievement of the target performance of the electrochemical devices.

In this review work, the following designations and abbreviations are used:

Abbreviations:

D — oxygen diffusion coefficient,
 DD — degradation degree,
 DR — degradation rate,
 MIECs — mixed ionic-electronic conductors,
 OCV — open circuit voltage,
 ORR — oxygen reduction reaction,
 PCFCs — protonic ceramic fuel cells,
 PCECs — protonic ceramic electrolysis cells,
 SOFCs — solid oxide fuel cells,
 SOECs — solid oxide electrolysis cells,
 TEC — thermal expansion coefficient,
 TG — thermogravimetry,
 TPB — triple phase boundary,
 WER — water evolution reaction,
 XRD — X-ray diffraction,
 sp. gr. — space group.

Symbols:

k — oxygen surface exchange constant,
 M — transition element,
 R — acceptor dopant,
 R_o — ohmic resistance,
 R_p — polarisation resistance,
 R_{total} — total resistance,
 P_{max} — maximal power density,
 p_{O_2} — oxygen partial pressure,
 $p_{\text{H}_2\text{O}}$ — water vapour partial pressure,
 T — temperature,
 r_A , r_B and r_O — ionic radii of A-, B- and O-ions, respectively,
 t — Goldschmidt's tolerance factor,
 α — the TEC value,
 δ — oxygen stoichiometry,
 η — overpotential.

Defect notation:

h^{\bullet} — electronic holes,
 e^{\bullet} — electrons,
 O_O^{\times} — oxide ion at the normal oxygen site,
 OH_O^{\bullet} — proton defects,
 $\text{R}'_{\text{Ce}(\text{Zr})}$ — acceptor dopant localised in the Ce(Zr) sublattice,
 $\text{V}_O^{\bullet\bullet}$ — oxygen vacancies.

Composition designations:

ABO_3 — perovskite structure,
 $\text{Ba}(\text{Ce}, \text{Zr})\text{O}_3$ — general system of the considered materials, BaCeO_3 – BaZrO_3 , which include boundary composi-

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Current research interest of the authors: energy conversion processes and technologies, designing solid oxide materials for high-temperature applications, fabrication and characterisation of solid oxide electrochemical systems (fuel cells, electrolysis cells, sensors, membrane reactors).

tions (BaCeO₃, BaZrO₃), solid solutions (BaCe_{1-x}Zr_xO₃) as well as doped or co-doped derivatives,

Ba(Ce,Zr,R)O₃ — same as above, but doped with R-dopant(s),

BCB — BaCe_{0.5}Bi_{0.5}O_{3-δ}
 BCCY — BaCo_{0.7}(Ce_{0.8}Y_{0.2})_{0.3}O_{3-δ},
 BCCY' — BaCe_{0.7}Co_{0.2}Y_{0.1}O_{3-δ},
 BCF — BaCe_{0.5}Fe_{0.5}O_{3-δ},
 BCFB — BaCe_{0.5}Fe_{0.3}Bi_{0.2}O_{3-δ},
 BCFBx — BaCe_{0.5}Fe_{0.5-x}Bi_xO_{3-δ} (x = 0, 0.1, 0.2 and 0.3)

BCFC — BaCo_{0.4}FeCe_{0.1}O_{3-δ},
 BCFZ — BaCo_{0.4}Fe_{0.4}Zr_{0.2}O_{3-δ},
 B_{0.9}CFZY — Ba_{0.9}Co_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-δ},
 BCFZY — BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-δ},
 BCP — BaCe_{0.6}Pr_{0.4}O_{3-δ},
 BCS — BaCe_{0.8}Sm_{0.2}O_{3-δ}
 BCSC — BaCe_{0.4}Sm_{0.2}Co_{0.4}O_{3-δ},
 BCSF — BaCe_{0.4}Sm_{0.2}Fe_{0.4}O_{3-δ},
 BCxFZ — BaCo_xFe_{0.7-x}Zr_{0.3}O_{3-δ} (x = 0.2, 0.3, 0.4 and 0.5),

BCFCG — BaCo_{0.4}Fe_{0.4}Ce_{0.1}Gd_{0.1}O_{3-δ},
 BCZY — BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-δ},
 BCZYYb — BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3-δ},
 BFCC — BaFe_{0.6}Co_{0.3}Ce_{0.1}O_{3-δ},
 BFSB — BaFe_{0.5}Sn_{0.2}B_{0.3}O_{3-δ},
 BSCF — Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ},
 BZY — BaZr_{0.8}Y_{0.2}O_{2-δ},
 BZCY35 — BaZr_{0.3}Ce_{0.5}Y_{0.2}O_{3-δ},
 BZCY442 — BaZr_{0.4}Ce_{0.4}Y_{0.2}O_{3-δ},
 BZCY63 — BaCe_{0.6}Zr_{0.3}Y_{0.1}O_{3-δ},
 BZC64 — BaZr_{0.6}Co_{0.4}O_{3-δ},
 BZCC — BaZr_{0.1}Ce_{0.7}Co_{0.2}O_{3-δ},
 BZF0.6Y — BaZr_{0.2}Fe_{0.6}Y_{0.2}O_{3-δ},
 BZF_xY — BaCo_{0.8-x}Fe_xY_{0.2}O_{3-δ} (x = 0.2, 0.4, 0.6 and 0.8),

LCSF — La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ},
 LSM — lanthanum strontium manganite, La_{1-x}Sr_xMnO_{3-δ},
 PBC — PrBaCo₂O_{5+δ},
 SDC — Ce_{0.8}Sm_{0.2}O_{2-δ},
 YSZ — yttria-stabilised zirconia, Zr_{1-x}Y_xO_{2-δ}.

2. General overview

2.1. Crystal structure features

The ABO₃ perovskite structure represents one of the largest bases for oxide materials utilised at elevated temperatures. The ABO₃ structure possesses a high flexibility allowing accommodation of different cations at the A- and B-site positions.³² As a result, all types of conductors (predominantly ionic, predominantly electronic, mixed ionic-electronic) can be formed depending on different charge combinations of basic cations (A⁺/B³⁺, A³⁺/B³⁺, A²⁺/B⁴⁺), as well as their redox behaviour and ionic radii.

In general, it is possible to evaluate the stability of perovskite structures using the Goldschmidt's tolerance factor (Eqn 1), which is based on the geometrical consideration of structural fragments of ABO₃.³³

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \quad (1)$$

where r_A, r_B and r_O are the corresponding radii of A-, B- and O-ions in the corresponding coordination states.

Using experimental data for a large number of oxide materials, it is found that the perovskite structure forms when the *t* value drops to within the range of 0.71–1.06. If this factor is close to 1.00, a cubic symmetry emerges; otherwise, different distortions of ABO₃ are observed with a deviation of *t* from unity.³⁴

BaCeO₃ and BaZrO₃ belong to the perovskite-structured materials (Fig. 1a). Barium as an alkaline-earth element with a large ionic radius occupies the A-site of ABO₃, being coordinated by twelve neighbouring oxygen ions. Cerium or zirconium, having lower ionic radii, is placed in the B-sublattice of ABO₃, where six oxygen ions form a B-centred octahedra. Using Shannon's ionic radii,³⁵ the *t* value of BaCeO₃ and BaZrO₃ amounts to 0.938 and 1.004, respectively. Under experimental conditions, a doped BaZrO₃ can be seen to adopt a cubic-type perovskite structure at room temperature (Fig. 1b), whose stability extends up to 1600 °C.³⁶ Conversely, an orthorhombic structure is most frequently observed for pure BaCeO₃, which, however, can transform to monoclinic, rhombohedral or even cubic structures at normal conditions depending on nature of

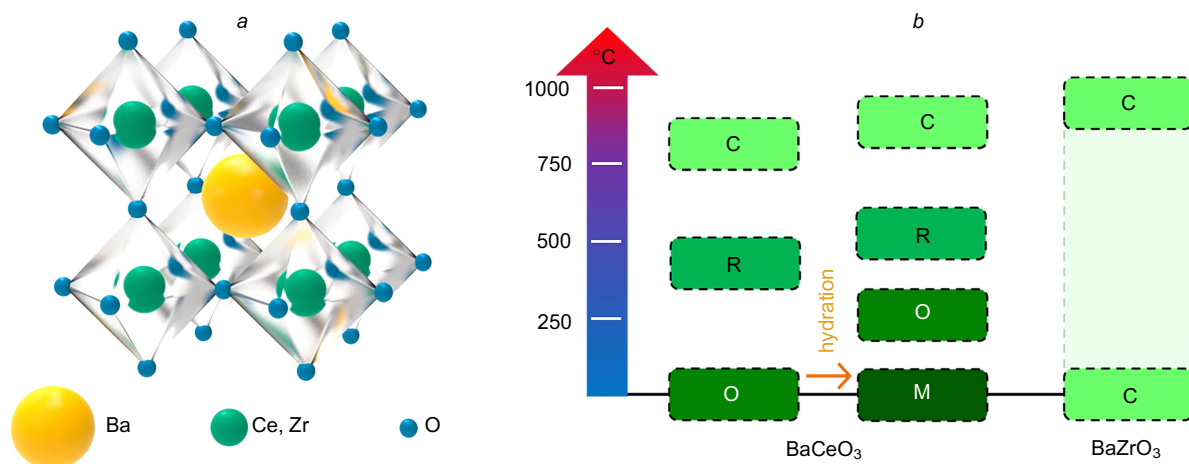


Figure 1. General perovskite structure of the Ba(Ce,Zr)O₃-based materials (a) and its evolution with heating (b). Abbreviations: M — monoclinic, O — orthorhombic, R — rhombohedral, C — cubic.

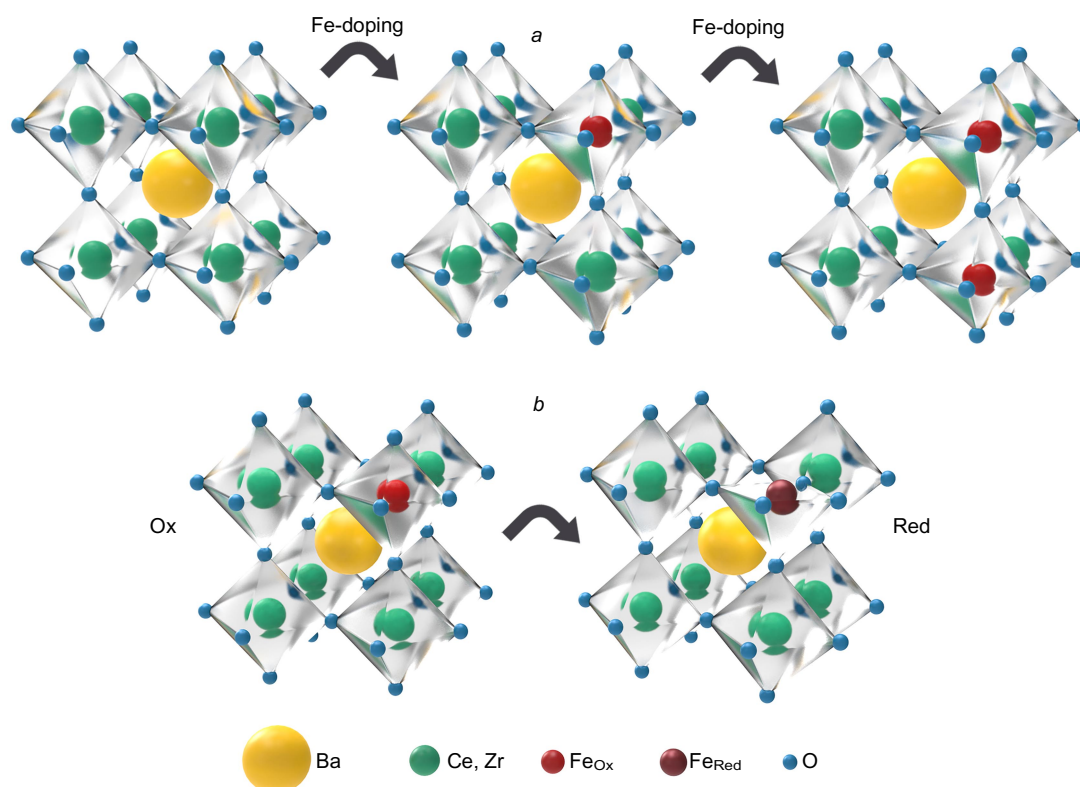
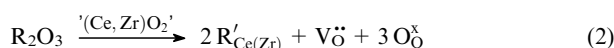


Figure 2. Schematic representations of the gradual Fe-doping of Ba(Ce,Zr)O₃ (a) and reduction of the obtained products (b).

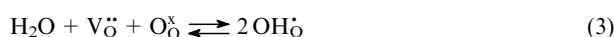
dopants, their concentration and/or degree of hydration (Fig. 1 b).^{37–39}

2.2. Defect chemistry

When BaCeO₃ or BaZrO₃ is doped with elements having a constant oxidation state ($R = Ln^{3+}, Sc^{3+}, In^{3+}, Y^{3+}$), a wide range of solid solutions can be formed. These oxides are used as a basis for designing electrolyte materials having a predominantly ionic conducting behaviour. In details, such a doping causes the formation of oxygen vacancies ($V_{\text{O}}^{\bullet\bullet}$):



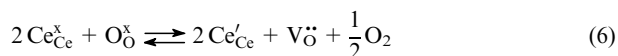
The oxygen vacancies compensate for the defects with an effective negative charge ($R'_{\text{Ce(Zr)}}$) and govern the oxygen-ionic transport of BaCeO₃- and BaZrO₃-based materials when these oxides are not significantly hydrated (low water vapour partial pressures, very high temperatures) or protonic transport (by means of proton defects, $\text{OH}_{\text{O}}^{\bullet}$) emerging in other cases, including at low temperatures coupled with high water vapour partial pressures:^{40–42}



Along with ionic transportation, cerates and zirconates show electronic transport on account of hole- (Eqn 4) or electron (Eqn 5) charge carriers, which can make a considerable contribution to overall transport under oxidising and reducing conditions, respectively.^{43–45}



On the basis of experimental results, p-type electronic conductivity can be seen to emerge at oxidising conditions above 500 °C and then rapidly increase with heating, starting to predominate over other partial (oxygen-ionic, protonic) conductivities at temperatures higher than 700–800 °C.⁶ Considering n-type electronic conductivity, it is possible that this originates under strongly reduced atmospheres (very low oxygen partial pressures, $p_{\text{O}_2}^{\dagger}$) on account of the partial reduction of Ce^{4+} -ions:



The equilibrium constant of this reaction varies from 10^{-42} at 400 °C to 10^{-17} at 800 °C, leading to a very low contribution of n-type electronic conductivity under real experimental conditions.⁴⁶

The total conductivity of the considered ceramic materials attains moderate values (not more than 0.1 S cm^{-1} at 900 °C)^{47,48} despite the gas compositions used. Due to this fact, the BaCeO₃- or BaZrO₃-based materials are mostly considered as electrolytes of protonic ceramic electrochemical cells. However, the electronic transport can be deliberately enhanced using elements with transition oxidation states (M), forming as-called mixed ionic-electronic conductors, MIECs.^{49–51} If the M-elements can substitute the basic ions of ABO₃ to form single-phase derivatives (Fig. 2 a), the transport properties of the materials depend

[†] Here and below partial pressures are provided in relative units (*i.e.* they are normalized to $P = 1 \text{ atm}$).

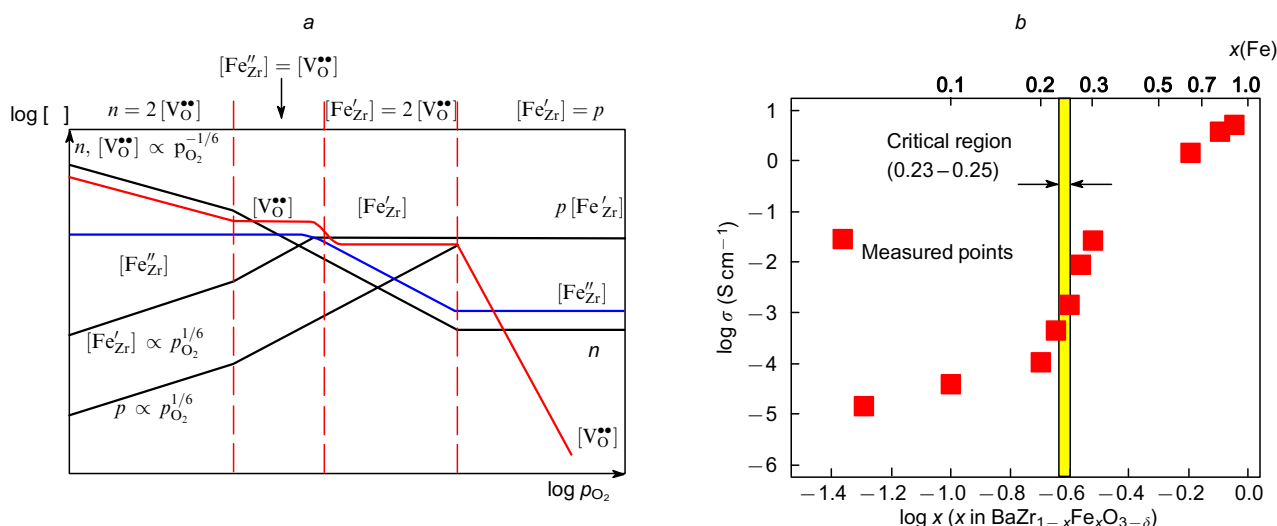
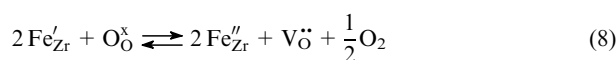
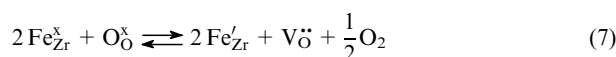


Figure 3. Transport properties of $BaZr_{1-x}Fe_xO_{3-\delta}$ materials: (a) concentrations of existing defects depending on oxygen partial pressure for $x = 0.1$ at $800\ ^\circ C$;⁵² (b) concentration dependence of the total conductivity obtained at $500\ ^\circ C$ in dry O_2 ($p_{O_2} = 1$).⁵⁴ Designations: $[]$ brackets denote concentration of defects, n is the concentration of electrons, p is the concentration of holes, $V_{O}^{\bullet\bullet}$ is the oxygen vacancy, Fe'_{Zr} is the Fe^{3+} -ion located at the zirconium sublattice of $BaZrO_3$, Fe''_{Zr} is the Fe^{2+} -ion located at the zirconium sublattice of $BaZrO_3$, p_{O_2} is the oxygen partial pressure, x is the level of Fe-doping of $BaZrO_3$, σ is the total conductivity.

on the charge conditions of M-ions, which are regulated by the external factors. For example, in the model $BaZr_{1-x}Fe_xO_{3-\delta}$ system, the Fe-ions can be consequently reduced by decreasing the oxygen partial pressure (Fig. 3a, ref. 52), forming first the Fe^{3+} -ions (Eqn 7) and then Fe^{2+} -ions (Eqn 8).



Here, Fe_{Zr}^x and Fe'_{Zr} are holes and electrons localised at the Fe'_{Zr} -ions. An additional equation (which is equivalent to the hole/electron interaction, null $\rightleftharpoons h^+ + e^-$) links all of these defects:



The reduction of the elements with transition oxidation states results in changes in the crystal structure (Fig. 2b, Ref. 53), consisting in chemical strain effects: an increase in the ionic radius of M-ions and removal of oxygen from its regular crystal position. Both of these outcomes affect the functional properties of the materials. For example, the conductivity caused by an increase in the concentration of electron charge carriers by doping with transition elements is not monotonic (Fig. 3b, Ref. 54). As a result of changes in the transportation mechanism, a percolation-type behaviour is observed: the p-type electron conductivity at low M concentrations is managed by transportation of holes localised at oxygen ions, while at higher M concentrations it is provided by holes localised at M-cations. Therefore, with a gradual growth of the M concentration, the total conductivity increases slightly⁵⁴ (or even decreases),^{55, 56} but then rises rapidly to reach $1 - 10\ S\ cm^{-1}$. From this perspective, the priority should be given the $Ba(Ce,Zr)O_3$ -based systems containing more than 40 mol. % of M in the Ce/Zr-positions.

2.3. Functional properties of oxygen (steam) electrodes

The electrode materials utilised in PCFCs or PCECs must fulfil strict requirements determining the overall performance of the electrochemical systems. There are various terms used to describe electrode performance: overpotential (η), area specific resistance or polarisation resistance (R_p). In this work, the latter term will be used for convenience. The R_p parameter depends on different factors,^{57–62} which can be categorised in two main groups (Fig. 4): chemical and morphological stabilities. In turn, these factors control (electro)catalytic activity of the electrode material as well as excellent exchange transport through the interfaces.

Chemical stability comprises all aspects of a material's stability, such as long-term tolerance, chemical compatibility with the electrolyte, electrode tolerance to poisoning by gas phase components, *etc.* The morphological stability group includes problems associated with the delamination process, coarsening of particles, *etc.* On the one hand, the mentioned drawbacks result in the deterioration of electrical contacts [decreasing triple phase boundary (TBP), active electrode area or porosity]; on the other hand, ionic and electronic current fluxes are also decreased. Various strategies can be deliberately utilised for the suppression of such undesirable processes.^{63–67} One of these is to develop

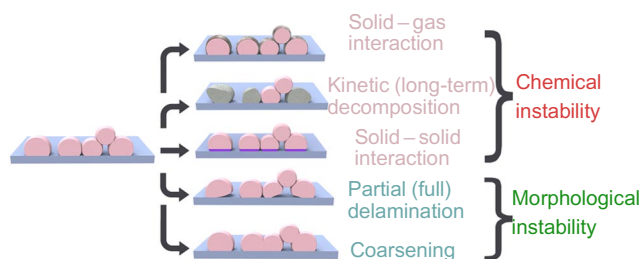


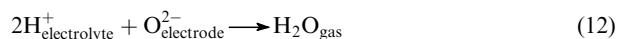
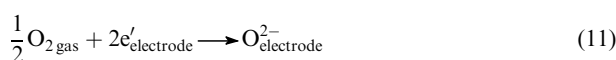
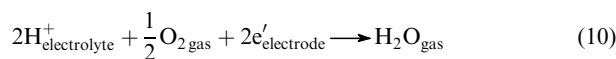
Figure 4. Possible reasons for increasing polarisation resistance of the electrodes in electrochemical systems.

electrodes having the same basic structure as the used electrolyte and consequently exhibiting a high chemical compatibility with it.

2.4. Justification for the design of Ba(Ce,Zr)O₃-based electrodes

The design of electrodes based on barium cerate or barium zirconate allows many problems to be overcome. Firstly, this approach can increase chemical compatibility since both functional [M-doped Ba(Ce,Zr)O₃ and R-doped Ba(Ce,Zr)O₃] materials are composed of the same structural fragments. In other words, the degree of possible interaction decreases considerably due to its being determined by the chemical activity of M- and R-cations with respect to each other. Thermal compatibility can also be improved by means of ensuring similar thermochemical strain responses. On account of their large perovskite structure, as well as the basic properties of Ba²⁺-, Ce⁴⁺- and Zr⁴⁺-cations, M-doped oxides might show hydration behaviour along with meaningful oxygen-ionic and electronic transport caused by M-cations. Such a combination opens new opportunities for the formation of single-phase triple-conducting materials, which are highly appreciated for their utilisation in protonic ceramic electrochemical cells.^{68–70} In detail, triple-conduction behaviour extends the electrochemical active sites from the TPB to the entire surface of the electrode particles, see Fig. 5.

As illustrated in Fig. 5a, in two protonic and electronic conductors when three phases of provided transportation of electrons (electrode), protons (electrolyte) and oxygen (gas atmosphere) exist simultaneously, the electrochemical reduction process is limited by the TPB region, see Eqn 10. In cases where MIECs are applied (Fig. 5b), the oxygen reduction stage occurs over the entire electrode surface (Eqn 11). However, the resulting water evolution reaction stage is still limited by the TPB length (Eqn 12). Eventually, the entire surface of the electrode becomes active towards both ORR and WER (Fig. 5c, Eqs. 10–13), extending the electrochemically active region from the length of the TPB to the surface of the double-phase boundary, *i.e.* the electrode's surface. However, in order to ensure sufficient rates of ORR and WER, the electrode materials should have high levels of each partial conductivity. Otherwise, the limiting cases (electronic conductors or MIECs) will be realised.



3. Functionality of the M-doped Ba(Ce,Zr)O₃ materials

Amongst the wide variety of oxide compositions, Ba(Ce,Zr)O₃ doped with praseodymium, cobalt and iron have been most thoroughly studied. Therefore, the main emphasis is devoted to such materials and their individual properties: phase structure, mechanical and chemical compatibilities, hydrogen capability and electrical conductivity.

3.1. Phase structure

The phase structure of the ABO₃ perovskites depends on numerous factors, including A and B matrix cations, concentration and type of dopants, their redox properties, cationic and anionic nonstoichiometry and even technological factors (temperatures of high-temperature treatments, dwelling times).^{32–34} When barium occupies the A-sublattice, while Ce or Zr occupy the B-sublattice, single-phase materials of BaCeO₃ having orthorhombic structure and BaZrO₃ with cubic structure are stable at room temperature, as discussed in detail in Section 2.1.

In case of Ba(Ce,Zr)O₃ doped with the M-transition elements, different results can be obtained in terms of the phase structure and purity of the obtained derivatives (see Table 1).

When Fe-doping is used with the BaCeO₃-based system, a limited range of solid solutions forms. According to numerous works,^{71, 72, 74, 75, 83} two ranges of solid solutions exist in the BaCe_{1-x}Fe_xO_{3-δ} system, which are limited by compositions with $x \approx 0.15$ and 0.85 . Such a low solubility limit can be explained by the high differences in ionic radii between the basic (Ce⁴⁺, $r_{\text{Ce}^{4+}}^{\text{VI}} = 0.87 \text{ \AA}$, here the superscript denotes the coordination state) and guest (iron, $r_{\text{Fe}^{4+}}^{\text{VI}} = 0.585 \text{ \AA}$, $r_{\text{Fe}^{3+}}^{\text{VI}} = 0.645 \text{ \AA}$) cations, which cause energetically unfavourable conditions. A similarly limited range for the heavy Fe-doped oxides ($0.85 \leq x \leq 1$) confirms this assumption. As shown by Eqn 1, a decrease in the average ionic radii of the B-ions leads to an increase in the tolerance factor; this implies that the overall stability of the perovskite structure (and its symmetry) should also increase, namely in the range of single-phase materials. Indeed, BaCe_{0.85}Fe_{0.15}O_{3-δ} has an orthorhombic perovskite structure,⁷⁵ while a hexagonal structure is detected for the nominal BaCe_{0.4}Sm_{0.2}Fe_{0.4}O_{3-δ} composition⁷¹ and BaCe_{0.15}Fe_{0.85}O_{3-δ} exhibits a cubic-type perovskite structure.⁷⁵

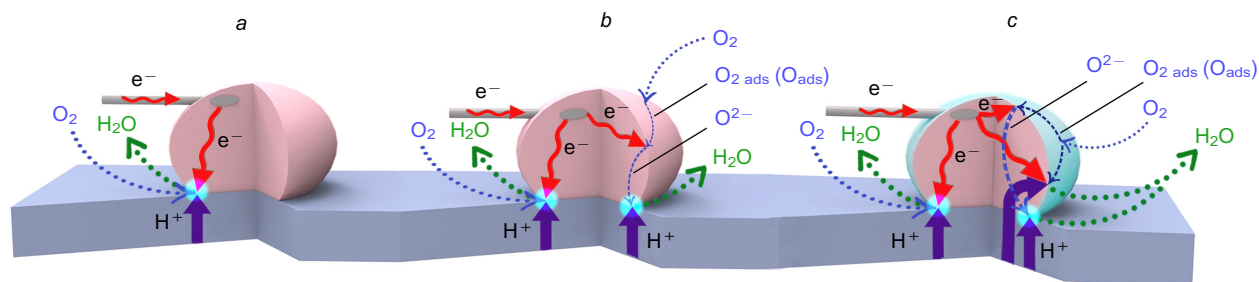


Figure 5. Simplified scheme of the electrochemically active sites in PCFCs with electronic (a), mixed oxygen-ionic/electronic (b) and triple (c) conducting electrodes. These sites are highlighted by a colour.