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Review of proton- and oxide-ion-conducting perovskite materials for SOFC applications

1 Kavitha Karuppiah MTEch

Senior Research Fellow, Functional Materials Laboratory, PSG Institute of Advanced Studies, Coimbatore, India

2 Anuradha M. Ashok PhD

Associate Professor, Functional Materials Laboratory, PSG Institute of Advanced Studies, Coimbatore, India; Associate Professor, Department of Physics, PSG College of Technology, Coimbatore, India (corresponding author: anu@psgias.ac.in)

In this review, the essential use of perovskites and their structural properties associated with proton and oxide-ion conductivity are explained specifically for applications in solid oxide fuel cells (SOFCs), electrolyser cells and so on. The number of oxygen vacancies and their distribution in the crystal structure play a crucial role in perovskites, which exhibit good protonic and oxide-ion conductivity. Atmospheric stability at the operating temperature is another important factor that decides the long-term usage of the materials. Here the properties are summarised in terms of stability, proton defects, ordering and cation substitution. A basic understanding of all of these properties will give a direction to synthesis of compounds with desired proton and oxide-ion conductivity for applications in renewable and sustainable energy devices. A certain group of perovskite oxides, when prepared as nanostructures, is specifically used in fuel cell electrodes for improved performance. A few trends and highlights of current scientific advances in nanoperovskites for energy applications are discussed. The high stability of the proton conductor $\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82}\text{O}_{8.73}$ and substitution of new dopants in this compound for SOFC devices are highlighted in this review.

Notation

r_A	ionic radius of the A-site cation
r_B	ionic radius of the B-site cation
r_O	ionic radius of the oxygen ion
t	tolerance factor

1. Introduction

The majority of the current energy systems that are mainly based on the combustion of fossil fuels cause many environmental problems such as air pollution, acid rain and greenhouse gas emissions. A significant amount of energy is also utilised for electricity generation and transportation, which is essential for daily life.¹ Due to increased industrialisation, the demand for energy, over-utilisation of energy resources and carbon dioxide (CO_2) emission have increased. Inefficient production and distribution of energy affects all sectors of the global economy. Major technological developments result in increasing energy demand. The quest for solutions to the deepening energy crisis points towards the question of how energy can be used on earth more efficiently and how to keep the environment clean. All efforts to solve these problems should include both conservation of energy resources and decrease in carbon dioxide emission.^{1,2} In this review, the authors report the role of perovskite oxides as proton and oxide-ion conductors in energy applications.

2. Perovskites

The mineral perovskite was discovered by Gustav Rose in 1839, and it was named after Russian mineralogist Lev Perovski. The name ‘perovskite’ was originally given to the mineral CaTiO_3 (calcium titanate).³ Perovskite-type oxides are the materials with the general formula ABO_3 , with the larger A cation coordinated to 12 anions and the B cation occupying six coordinate sites, forming a network of corner-sharing BO_6 octahedra, as shown in Figure 1. The larger A cations can be rare-earth elements – alkaline earth or alkali⁴ – whereas the smaller B cations include transition metals. The ionic radii and valence of cations determine the distortions present in the crystal structure, which in turn are responsible for the chemical and physical properties of the materials.⁴ This type of perovskite oxide materials, due to their adaptability, are extensively studied and used for a wide range of applications. Materials with the perovskite structure are desirable due to their unique properties such as catalytic behaviour, ferroelectricity, thermoelectricity, magnetic properties, oxide-ion conduction and proton conduction^{5–8} that are useful in gas sensors, gas separation membranes, thermal barriers, solid oxide fuel cell (SOFC) electrolytes and so on. Moreover, materials with the perovskite structure, when compared to materials with other crystal arrangements, generally exhibit good stability. Appropriate selection of A and B cations, to maintain suitable defects such as

Figure 1. General cubic structure of the ABO_3 perovskite oxides

oxygen vacancies and non-centrosymmetry, makes them suitable for many solid-state device applications.

2.1 Stability of perovskites

The stability of the perovskite structure is determined in terms of the Goldschmidt tolerance factor developed in the 1920s based on the following equation

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

In the above equation r_A , r_B and r_O are the ionic radii of the A-site cation, B-site cation and oxygen ion, respectively. The stable perovskite structure is expected to have $0.77 \leq t \leq 1$.^{9,10} Tuning the t value close to unity with appropriate choices of A and B cations results in high-symmetry crystal structures with a small unit cell volume.¹¹ For a perfect cubic structure, the value of the tolerance factor is equal to 1 ($t = 1$). It is obtained by selecting the size of the A-site cation to be closer to that of the oxygen ion (1.40 Å). In a perfect cubic perovskite structure, the B–O–B chains are linear with a bond angle of 180°. When the crystal structure varies from cubic to another symmetry, the bond angle of B–O–B chains will be reduced. For $t > 1$, the hexagonal structures tend to be stable,⁹ whereas for $t < 1$, the lattice structure changes from cubic to rhombohedral and then to orthorhombic.^{10,12} Figure 1 represents an A-cation-centred view of the basic cubic perovskite.

2.2 Cation substitution in perovskites

It is well known that the specific properties of perovskite materials are tailored by suitable cation substitution. Appropriate substitution of cation material helps in the enhancement of magnetism, electrical conductivity, surface area, mechanical

strength and catalytic reactivity.^{10,13} The variations of such properties generally result from the B cations, but are tuned by the A-site cations. Factors such as the ionic radius of the A cation and its valence control stability and other properties.¹⁴ For example, when lower-valence dopants are substituted in the cationic site, oxygen vacancies are introduced within the perovskites, which further enhance specific properties such as ionic conductivity.¹⁰ Depending on the nature of the material, the dopant can drastically affect the band structure and hence the electronic properties can also be changed. The partial cation substitution in the A and B sites with divalent elements (calcium (Ca), strontium (Sr) and barium (Ba)) will result in significant changes on oxygen diffusion and the surface exchange coefficients of those perovskite materials which can be used in oxygen semi-permeable membranes.¹⁵ In perovskite-type oxide, the partial substitution at the A site with another metal cation strongly influences the catalytic activity due to the stabilisation of B cation oxidation states and the formation of structural defects. The structural defects are responsible for catalytic activity and oxygen mobility within the solid crystal lattice due to the non-stoichiometry created by the substitution.¹⁶ For example, the progressive substitution in the B-site position of iron (III) (Fe^{3+}) by nickel (II) (Ni^{2+}) in $La_{0.6}Ca_{0.4}Fe_{1-x}Ni_xO_3$ entails the progressive formation of oxygen vacancies. The highest catalytic properties are found for the compound with more oxygen vacancies.¹⁶

Cation substitution also introduces oxygen vacancies into such perovskite oxides by enhancing the mixed (oxygen) ionic–electronic conductivity and reduction–oxidation (redox) properties,¹⁷ which are beneficial for applications in SOFCs, oxygen-permeable membranes, metal–air batteries and electrochemical water (H_2O) splitting.^{18–21} In the type of perovskites explained in the next section, although perovskites are stoichiometric and chemically neutral, oxygen vacancies can be formed due to the insufficient oxygen atoms provided by the stoichiometric perovskite to occupy the available oxygen sites in the crystal structure.²²

2.3 Non-stoichiometric $A_3B'B''_2O_9$ complex perovskite as proton and oxide-ion conductors

Complex perovskites of type $A_3B'B''_2O_9$, where A and B' = alkaline-earth metal and B'' = niobium (Nb) and tantalum (Ta), are found to have the interesting property of mixed proton and oxide-ion conductivity and were first observed in the early 1990s.^{22,23} This type of complex perovskite has a wide range of applications as electrolytes in fuel cells, electrolyzers, batteries, sensors and so on.^{24–26} Several compositions of $A_3B'B''_2O_9$ -type complex perovskites have been extensively studied because of the possibility of creating effective negative charges by varying the ratio between B' and B'' ion concentrations.²⁶ From the structural point of view, $A_3B'B''_2O_9$ is different from the ABO_3 perovskite structure: it contains a mutually compensating mixture of pentavalent and divalent cations in the B-site sublattice.²² The large valence difference makes the two B cations ordered.²⁷ The variation in the ratio between B' and B'' ions makes the

perovskite stoichiometric or non-stoichiometric. For example, the $\text{Ba}_3\text{Ca}_{1+x}\text{Nb}_{2-x}\text{O}_{9-3x/2}$ perovskite series has two types of ordering: 1:1 and 1:2, based on the ratio between B' and B'' ions.^{22,23,28,29} When $x = 0$, the aforementioned composition becomes $\text{Ba}_3\text{Ca}_1\text{Nb}_2\text{O}_9$, in which calcium and niobium atoms are in the ratio 1:2. With this arrangement, the material has a crystal structure with trigonal symmetry with no structural oxygen vacancies. The calcium atoms are arranged in one layer and the niobium atoms in two layers along the c -axis of the trigonal unit cell as described earlier.¹⁹ When $x = 0.5$, the composition becomes $\text{Ba}_3\text{Ca}_{1.5}\text{Nb}_{1.5}\text{O}_{8.25}$, in which calcium and niobium atoms are in the ratio 1:1, having a crystal structure with cubic symmetry with two oxygen-deficient sites. This structure has alternate layers of calcium and niobium atoms along the body diagonal of the cubic unit cell.^{25,26} Later Nowick *et al.*²³ and Norby²⁴ studied various compositions of $\text{Ba}_3\text{Ca}_{1+x}\text{Nb}_{2-x}\text{O}_{9-3x/2}$ perovskite ($x = -0.03, 0.0, 0.03, 0.09, 0.18, 0.4$ and 0.36). For $x = -0.03$ and 0.0 , the compound showed 1:2 ordering; $x = 0.03$ showed both 1:1 and 1:2 ordering, and for $x = 0.09$ and above, the compound showed 1:1 ordering. From this observation, it is revealed that introducing non-stoichiometry induces a 1:2 to 1:1 structural order transformation.²⁶ These types of complex perovskites behave as proton conductors in wet atmospheres at lower temperatures and oxide-ion conductors in dry atmospheres at higher temperatures.²⁹

3. Proton conductivity in doped perovskites

Iwahara *et al.*³⁰ published the first report on proton conduction in perovskites in the 1980s. They studied cerates of barium (BaCeO_3) and strontium (SrCeO_3) systems and observed high levels of proton conductivity (10^2 – 10^{-3} S/cm, 600–1000°C).³⁰ After 20 years of intense research, the perovskite-type cerates and zirconates have become well-known proton conductors.^{31–33} Later, other perovskite oxides were also found to show a good response against proton conduction. One of the best-known perovskite proton conductors is $\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82}\text{O}_{8.73}$ (BCN 18), which displays a combination of high proton mobility and relatively high proton concentration. This exhibits proton conductivities close to 10^{-3} S/cm.²⁹ This compound is a result of introducing non-stoichiometry into the parent perovskite oxide to obtain desirable defects such as oxygen vacancies.

3.1 Protonic defects in perovskites

In perovskite oxides at moderate temperatures, the formation of protonic defects occurs by dissociative absorption of water, which requires the presence of oxide-ion vacancies $V_{\text{O}}^{\bullet\bullet}$. The vacancies are formed either intrinsically by varying the ratio of main constituents in the composition or extrinsically by acceptor doping.²⁷ The oxygen vacancies formed incorporate the protons into the material as shown in Figure 2. When these materials are exposed to humid atmospheres, the water molecule in the gas phase dissociates into a hydroxide ion and a proton.³⁴ The hydroxide ion sits on the oxide-ion vacancy and the protons occupy the interstitial sites of the perovskite lattice. This phenomenon is explained as follows

Figure 2. Proton conduction mechanism in perovskite oxide

where $V_{\text{O}}^{\bullet\bullet}$ is the Kröger–Vink notation for an oxygen vacancy; $\text{O}_{\text{O}}^{\text{x}}$ is an oxide ion; and $\text{OH}_{\text{O}}^{\bullet}$ is a proton attached to an oxide ion. The protons thus introduced may move around in the crystal by jumping from one oxygen atom to another.

Under reducing conditions (low oxygen partial pressure), the sample may lose oxygen and form electrons as given in the equation below

The oxidising conditions (high oxygen partial pressure) result in the formation of electronic holes ($h^\bullet$)

4. Oxide-ion-conducting perovskites

Oxide-ion conductors have been widely used in fuel cells, oxygen sensors, oxygen pumps and oxygen-permeable membrane catalysts.^{35–38} Most of these applications require a high temperature to achieve high oxygen flux for efficient operation. Perovskite is one class of material exhibiting high oxide-ion conduction.³⁵ To be an oxide-ion conductor, the essential feature is the presence of oxygen vacancies. Doping is usually performed by substituting a lower-valence cation into the lattice, with the added effect of introducing oxygen vacancies to maintain overall charge neutrality.³⁹ These oxygen vacancies supply the equivalent

sites, allowing the oxygen ions to migrate, thus facilitating ionic conductivity. The oxide-ion conduction mechanism in a non-stoichiometric perovskite with a double-perovskite structure (e.g. $\text{Ba}_4\text{Ca}_2\text{Nb}_2\text{O}_{11}$) is described in Figure 3.

At a high temperature, due to the lattice vibrations and chemical potential gradient, oxide ions move to the nearby oxygen vacancies. Further, the vacancy created by the movement of one oxide ion will be occupied by another neighbouring oxide ion. This movement is a result of thermally activated hopping of the oxide ions, moving from one crystal lattice site to a neighbouring lattice site, with a superimposed drift in the direction of the electric field. The oxygen ions are the largest components of the lattice, with an ionic radius of $1.4 \text{ \AA}$.³⁹ It is expected that smaller-ionic-radius metals have appreciable mobility in the lattice with enhanced conductivity.

Well-known oxide-ion conductors are yttria-stabilised zirconia (YSZ), cerium gadolinium oxide (CGO), $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$ (LSGM), $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ (silicon (Si)-apatite), $\text{La}_2\text{Mo}_2\text{O}_9$ and $\text{Bi}_2\text{V}_{1.8}\text{Cu}_{0.1}\text{O}_{5.35}$.^{40,41} These oxides exhibit higher oxide-ion conductivity on the order of 0.1 S/cm . YSZ and CGO are commercially available oxide-ion conductors used for SOFC electrolyte material. LSGM is a perovskite-based oxide-ion conductor exhibiting higher ionic conductivity than the fluorite YSZ. In terms of activation energy, mixed conducting materials exhibit lower activation energy ($\sim 0.25 \text{ eV}$), whereas oxide-ion conductivity requires higher activation energy ($\sim 0.6\text{--}1.2 \text{ eV}$).⁴²

5. BCN proton-oxide-ion conductor

Complex perovskites of type $\text{A}_3(\text{B}_{1+x}\text{B}'_{2-x})\text{O}_{9-3x/2}$, where A and B = alkaline-earth metals and B' = niobium or tantalum ($0 < x \leq 0.5$)

Figure 3. Oxide-ion conduction in non-stoichiometric perovskite oxide

exhibit high oxide-ion conductivity in dry atmospheres ($>400^\circ\text{C}$, higher temperatures) and proton conductivity in hydrated atmospheres ($<400^\circ\text{C}$, lower temperatures).^{22,23,43} In recent years, such ceramic oxides have been extensively studied due to their high proton conductivity ($5.3 \times 10^{-3} \text{ S/cm}$) at intermediate temperatures ($500\text{--}750^\circ\text{C}$) with a low activation energy of $\sim 0.54 \text{ eV}$.⁴⁴ These intermediate-temperature proton conductors are widely used in diverse applications.^{8,45,46} Among different types of proton-conducting ceramics, cerates are found to exhibit the highest proton conductivity of $1.0 \times 10^{-2} \text{ S/cm}$.^{44,47,48} However, cerates readily decompose in carbon dioxide or humid atmospheres and thus exhibit thermodynamic instability.⁴⁴ Later, cerium (Ce) partially replaced zirconium (Zr) ions to improve their stability. Zirconium substitution in cerates provided good stability, but their total conductivity was greatly reduced.^{49,50} In order to improve the stability and conductivity of proton conductors, many research groups started working on other alternate oxides. Among many ceramic oxides, the cation off-stoichiometric complex perovskite $\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82}\text{O}_{9-\delta}$ (BCN 18) exhibits a high transport number close to unity in reducing atmospheres⁵¹ with proton conductivity of around 0.1 S/cm in a water atmosphere. BCN 18 also exhibits high structural and chemical stability against carbon dioxide and humidified atmospheres.⁵² $\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82}\text{O}_{9-\delta}$ was originally derived from $\text{Ba}_3\text{CaNb}_2\text{O}_9$, which is a 1:2-ordered perovskite type.²³ $\text{Ba}_3\text{CaNb}_2\text{O}_9$ is an insulator with no structural oxygen vacancies with B-site ordering blocking the movement of the ionic defects. By making the calcium ion (Ca^{2+}) off-stoichiometry ($\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82}\text{O}_{9-\delta}$), oxygen vacancies are created, which facilitates the proton/oxide-ion conductivity.⁴⁴ BCN 18 with modified B-site ordering is mostly synthesised by using the solid-state method. Few researchers studied the electrical properties of $\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82}\text{O}_{9-\delta}$ prepared by using the combustion method.⁵³ It was revealed that dopants in the niobium site could improve the proton conductivity without sacrificing chemical stability.⁵⁴ Oxygen-deficient $\text{Ba}_4\text{Ca}_2\text{Nb}_2\text{O}_{11}$, a 1:1-ordered compound, nominally has a higher concentration of oxygen vacancies than BCN 18.²⁹ The proton and oxide-ion conductivity of $\text{Ba}_4\text{Ca}_2\text{Nb}_2\text{O}_{11}$ was studied and compared with that of $\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82}\text{O}_{9-\delta}$. It is observed that, even though a higher concentration of oxygen vacancies is present in $\text{Ba}_4\text{Ca}_2\text{Nb}_2\text{O}_{11}$, it does not show better results because the increasing concentration of oxygen vacancies reduced the oxygen ion mobility.²⁹ It is observed that $\text{Ba}_4\text{Ca}_2\text{Nb}_2\text{O}_{11}$ in dry air retains its cubic crystal structure with space group $Fm\bar{3}m$ having structural oxygen vacancies. However, when it is annealed in wet air, its crystal structure changes to monoclinic with space group $C2/m$ due to water incorporation in vacancies.^{26,29} The change in the ratio between barium and calcium greatly influences the electrical properties of perovskite ($\text{Ba}_{1-x}\text{Ca}_x$) $_6\text{Nb}_2\text{O}_{11}$ ($0.23 \leq x \leq 0.47$) solid solutions.⁵⁵ It is also observed that the increase in barium content decreases oxide-ion and proton conductivity.⁵⁵ As said earlier, doping in the niobium site has proven to enhance the electrical properties.⁵⁴ Therefore, research has been focused towards doping different elements in the niobium site. Because of doped non-metallic phosphate in the proton conductor $\text{Ba}_4\text{Ca}_2\text{Nb}_2\text{O}_{11}$, it is found that oxoanion

substitution enhances the chemical stability in a carbon dioxide atmosphere.⁵⁶ Doping new elements to increase conductivity should not affect chemical stability, which in turn affects performance. Several elements such as tantalum, titanium (Ti), iron, manganese (Mn), cobalt (Co) and potassium (K) are doped in the proton conductor $\text{Ba}_3\text{Ca}_{1-x}\text{Nb}_{2-x}\text{O}_{9-\delta}$ (BCN) to enhance the number of oxygen vacancies and also to maintain chemical stability.^{57–60} The effect of potassium on the electrical properties of 1:1-ordered BCN proton conductor was studied, and it was found that better conductivity and chemical stability can be achieved when 25% of the barium sites are replaced by potassium ions.⁶¹ The effects of cerium and yttrium (Y) doping on the calcium and niobium ions in complex perovskite $\text{Ba}_3\text{Ca}_{1-18}\text{Nb}_{1-82}\text{O}_{9-\delta}$ proton conductor was also studied.^{44,46} Such doping demonstrated new directions in the development of new materials for intermediate-temperature proton conductors with high conductivity and good stability. The doped compositions of BCN perovskite and their conductivity values are listed in Table 1. It is observed in the table that doping in BCN perovskite improves both conductivity range and stability, making it even more suitable for SOFC devices.

6. Role of nanoperoovskites in SOFCs

SOFCs have gained increasing attention over the past few decades because of their likely applications in lowering industrial pollutant emission and increasing energy efficiency.^{63–67} However, a number of problems, such as unsatisfactory redox stability, remain to be solved prior to the large-scale industrial application of the technology. Nanostructured materials have extensive applications in such devices due to their size-reduction properties. Perovskite materials synthesised as nanoperoovskites with an increased surface area-to-volume ratio, which in turn increases the active electrode area, can be used in oxygen separation membranes, sensors, SOFCs and so on. The use of nanomaterials in SOFCs is directed towards (a) lowering the temperature of operation of the cell (down to 300–400°C), (b) retaining phase/thermal stability, (c) achieving the essential level of conductivity (0.1 S/cm), (d) introducing tolerance to sulfur, (e) avoiding carbon deposition on the anode when hydrocarbon fuels are used and so on.^{68,69}

Table 1. Conductivity of BCN and doped BCN

Composition	Conductivity: S/cm
$\text{Ba}_3\text{Ca}_{1-x}\text{Nb}_{2-x}\text{O}_{9-\delta}$	5.5×10^{-4} at 600°C (air) ²⁴
$\text{Ba}_2(\text{Ca}_{0.9}\text{Nb}_{0.66}\text{Ta}_{0.55})\text{O}_{6-\delta}$	5.0×10^{-4} at 400°C (wet) ⁵⁷
$\text{Ba}_3\text{Ca}_{1-18}\text{Nb}_{1-57}\text{Ti}_{0-25}\text{O}_{8-605}$	3.5×10^{-4} at 400°C (wet) ⁵⁸
$\text{Ba}_2\text{Ca}_{0.79}\text{Co}_{0.5}\text{Nb}_{0.71}\text{O}_{6-\delta}$	3.7×10^{-2} at 816°C (air) ⁵⁹
$\text{Ba}_2\text{Ca}_{0.79}\text{Mn}_{0.5}\text{Nb}_{0.71}\text{O}_{5-09}$	7.74×10^{-4} at 600°C (air) ⁵⁹
$\text{Ba}_2\text{Ca}_{0.67}\text{Fe}_{0.33}\text{NbO}_{5-66}$	7.82×10^{-4} at 600°C (air) ⁵⁹
$\text{Ba}_{1-75}\text{K}_{1-25}\text{CaNb}_2\text{O}_{9-\delta}$	1.0×10^{-3} at 700°C (dry hydrogen gas (H_2)) ⁶⁰
$\text{Ba}_4\text{K}_4\text{Ca}_4\text{Nb}_4\text{O}_{20}$	3.79×10^{-5} at 800°C (air) ⁵¹
$\text{Ba}_3\text{Ca}_{1-18}\text{Nb}_{1-77}\text{Ni}_{0-05}\text{O}_{9-\delta}$ (BCNNi)	2.6×10^{-3} at 700°C (wet air) ⁶²
$\text{Ba}_3\text{Ca}_{1-18}\text{Nb}_{1-52}\text{Y}_{0-3}\text{O}_{9-\delta}$ (BCNYO-3)	5.3×10^{-3} at 600°C (wet air) ⁴⁴
$\text{Ba}_3\text{Ca}_{1-18}\text{Nb}_{1-62}\text{Ce}_{0-2}\text{O}_{9-\delta}$	2.69×10^{-3} at 550°C (wet hydrogen gas) ⁴⁶

The surface area obtained from nanostructured materials is several times higher than that of bulk materials. This increases the triple-phase boundary and enhances the electrochemical performance of SOFCs.⁷⁰ The reduction in particle size is also expected to reduce the operating temperature, which is a major limitation ascribed to sintering processes. Overall, the use of nanomaterial layers reduces the working temperature with enhanced cell performance. Specifically, the major challenge with regard to the electrolyte layer of SOFCs is to make a thin layer of electrolyte without sacrificing structural integrity and other characteristics. The grain growth of nanostructured ionic conductors is also suppressed by adding another phase into an interparticle region. Such composite nanostructured electrolytes show prominent conductivity enhancement.⁷¹ With these advantages, nanoperoovskites are expected to play an important role in the fabrication of novel SOFCs for clean energy generation.

6.1 BCN for SOFCs and other applications

As described earlier, BCN and doped BCN are used in a wide range of applications such as SOFCs, gas separation membranes and sensors. Since BCN 18 shows remarkable chemical stability in carbon dioxide and humid atmospheres, it can be used for practical applications, but its relatively low conductivity hinders its usage in certain applications. It is observed that doping cerium (IV) (Ce^{4+}) in BCN 18 showed significant enhancement of electrical properties along with better chemical stability.⁴⁶ Among compositions with different cerium dopant concentrations, the composition $\text{Ba}_3\text{Ca}_{1-18}\text{Nb}_{1-62}\text{Ce}_{0-2}\text{O}_{9-\delta}$ exhibited higher proton conductivity of 2.69×10^{-3} S/cm at 550°C and good stability in the intermediate-temperature range. Its thermal expansion coefficient is $14.73 \times 10^{-6} \text{ K}^{-1}$ in air and $15.03 \times 10^{-6} \text{ K}^{-1}$ in 5% hydrogen gas (H_2).⁴⁶ An SOFC single cell was fabricated using a two-step sintering method using BCN 18 as electrolyte, and its performance was studied.⁷² The maximum power density obtained was about 106 mW/cm² at 750°C compared to earlier reported power densities. A maximum power density obtained using BCN 18 as electrolyte, prepared by using an in situ method, was 48 mW/cm² at 700°C.⁵⁴ The effect of partial substitution of niobium ions by yttrium ions ($\text{Ba}_3\text{Ca}_{1-18}\text{Nb}_{1-52}\text{Y}_{0-3}\text{O}_{9-\delta}$) showed a proton conductivity value of 5.3×10^{-3} S/cm at 600°C with cell power output of 103 mW/cm² at 750°C.⁴⁴ The power outputs of devices fabricated using doped and undoped BCN as electrolyte are listed in Table 2. It can be noticed from the table that the highest power output reported so far was obtained when using BCN 18 as electrolyte and nickel– $\text{Ba}_3\text{Ca}_{1-18}\text{Nb}_{1-82-x}\text{Y}_x\text{O}_9$ (BCZYYb)/ $\text{BaCo}_{0-7}\text{Fe}_{0-2}\text{Nb}_{0-1}\text{O}_{3-\delta}$ (BCFN) as electrodes.

The crystal structure of perovskite materials, when synthesised as nanoperoovskites, varies based on the type of dopant and arrangement of defects.⁷⁵ The defects formed on the surface play an essential role in the tuning of many properties other than proton and oxide-ion conductivity. These properties provide a wider scope of applications other than in SOFCs, such as in gas sensors; piezoelectric, ferroelectric, dielectric, optical and pyroelectric devices; thermistors; multilayer ceramic capacitors;

Table 2. Conductivity and SOFC studies of BCN and doped BCN perovskites

Electrolyte	Electrolyte thickness: μm	Anode	Cathode	Power output: mW/cm^2	Conductivity (σ): S/cm
BCN ⁷³	1000	Platinum (Pt)	Platinum	0.4	1.51×10^{-3}
BCN ⁵⁴	15	Ni-BCN	LSF	48	1.51×10^{-3}
BCN ⁷⁴	25	Ni-BCN	BCFN	46	1.51×10^{-3}
BCN ⁷⁴	25	Ni-BCZYYb	BCFN	97	1.51×10^{-3} (wet hydrogen gas)
BCN ¹⁸⁴⁶	25	Ni-BCZYYb	BCFN	106	2×10^{-3} (air)
BCNNi ⁶²	45	Ni-BCNNi	PBCO	84	4.59×10^{-3}
BCNYO ₃ ⁴⁴	Not mentioned	Ni-BCZYYb	Platinum/air	103	5.3×10^{-3}

LSF, $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_{3-\delta}$; PBCO, $\text{PrBaCo}_2\text{O}_{5+\delta}$

pressure sensors; and hydrogen sensors.^{76–78} Recent studies stated that the negligible release of thorium in seawater from Greek bauxite residue is found due to its incorporation into an insoluble perovskite-type phase with major composition of $\text{Ca}_{0.8}\text{Na}_{0.2}\text{TiO}_3$ and crystallites observed at the nanoscale.⁷⁹ However, when nanoperovskite is used as sintered ceramic, the resistance to ion migration offered by the grain boundaries is one of the major challenges which need to be addressed during device fabrication.

7. Conclusion

In this review, the essential role of oxygen vacancies in perovskite oxides with associated proton and oxide-ion-conducting properties is discussed. Cation ordering in BCN perovskite decides the nature and the number of oxygen vacancies, which are also the sources of protonic defects. Doped and undoped BCN, with 1:1-ordered B-site cation sublattice, behave as both proton (wet atmosphere–low temperature) and oxide-ion conductors (dry atmosphere–high temperature). The role of BCN in SOFCs is discussed in detail. Using suitable dopants in BCN proton conductors can widen their applications in many other devices for energy applications.

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