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TOPICAL REVIEW

Roadmap on inorganic perovskites for energy applications

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Keywords: perovskites, energy, solar fuels, catalysis, fuel cells, thermoelectrics, water splitting

Abstract

Inorganic perovskites exhibit many important physical properties such as ferroelectricity, magnetoresistance and superconductivity as well their importance as energy materials. Many of the most important energy materials are inorganic perovskites and find application in batteries, fuel cells, photocatalysts, catalysis, thermoelectrics and solar thermal. In all these applications, perovskite oxides, or their derivatives offer highly competitive performance, often state of the art and so tend to dominate research into energy material. In the following sections, we review these functionalities in turn seeking to facilitate the interchange of ideas between domains. The potential for improvement is explored and we highlight the importance of both detailed modelling and *in situ* and operando studies in taking these materials forward.

Contents

Introduction

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The perovskite structure is a relatively simple atomic arrangement based upon a stoichiometric ABX_3 array with two cation sites and one anion site. The smaller B cation can be viewed as occupying interstices in an approximately close packed array of AX_3. In its primitive form the lattice is face centred cubic with the B ions being octahedrally coordinated to the X anions. Despite its relative simplicity this structure type presents an exceptional variety of important properties that are highly tuneable and is often termed an inorganic chameleon. This great functionality is built upon the important B-X framework and its high degree of covalency, figure 1. The tunability arise from a great deal of elemental flexibility and especially a high degree of substitutional flexibility and non-stoichiometry.

There has been much recent interest in the hybrid perovskites with a lead halide inorganic component and with an organic cation for their impressive photovoltaic properties. Whilst these undoubtedly share the same structural motif as inorganic perovskites, there are important differences in structural character. Thus inorganic perovskites, especially oxides (i.e. $X = O$) might be considered as the true perovskites. Certainly, inorganic perovskites are the parent structures with the mineral Perovskite being discovered in 1839 and named after Count Perovski, with its oxide structure being understood nearly 100 years ago. Here, we seek to revisit these inorganic perovskites and bring together the state of the art on their important functionalities.

Inorganic perovskites exhibit many important physical properties such as ferroelectricity, magnetoresistance and superconductivity as well their importance as Energy Materials. Many of the most important energy materials are inorganic perovskites and find application in batteries, fuel cells, photocatalysts, catalysis, thermoelectrics and solar thermal conversion. In all these applications, perovskite oxides, or their derivatives offer highly competitive performance, often state of the art and so tend to dominate research into energy material. In the following sections, we review these functionalities in turn seeking to facilitate the interchange of ideas between domains. The potential for improvement is explored and we highlight the importance of both detailed modelling and *in situ* and operando studies in taking these materials forward. The inter-relationships between these various functions and their governing properties are highlighted in the following scheme.

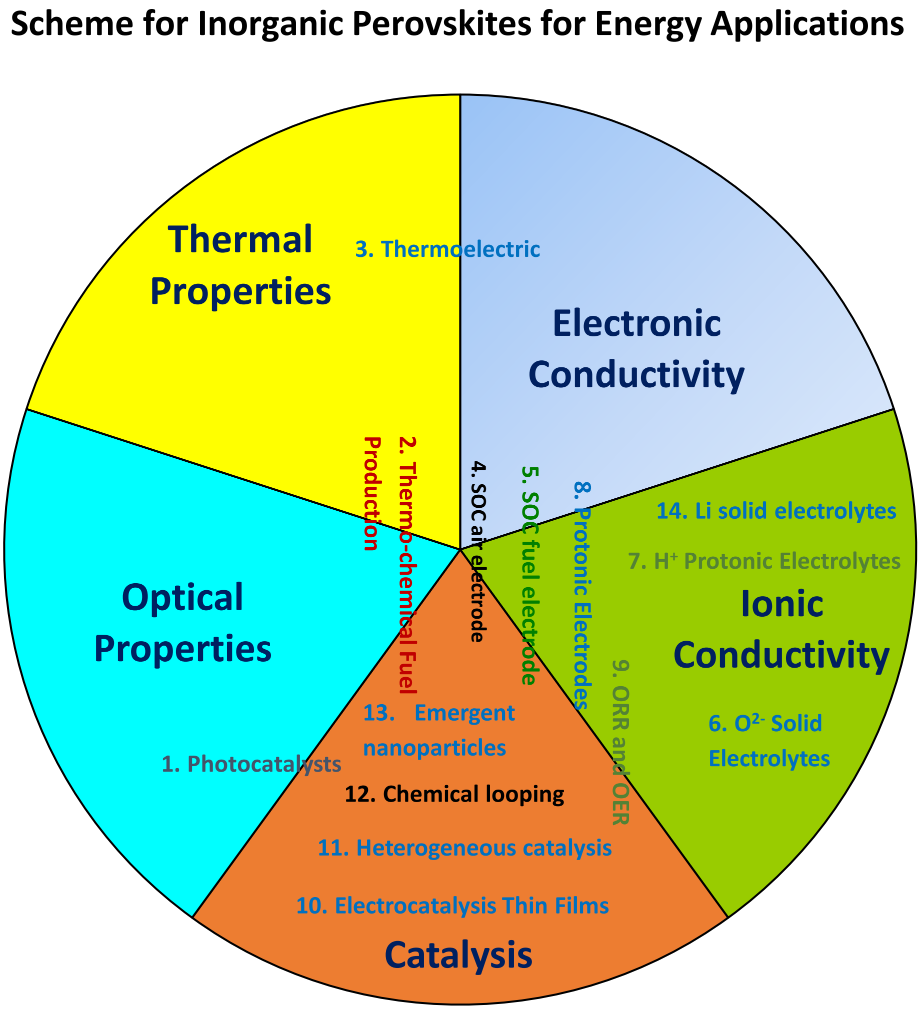

Figure 1. Representation of application fields and their tie to specific properties for inorganic perovskites in energy applications. The numbers refer to the according sections to direct the reader for thematic reads through this article.

1. Photocatalysts for water splitting

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1.1. Status

Owing to the clean nature of hydrogen as an energy carrier, splitting water to generate hydrogen using renewable energy as sunlight or electricity from sunlight/wind has been actively pursued in the past half century worldwide. As a flagship example for this purpose, water splitting on particulate photocatalyst holds great promise for hydrogen production due to its technical simplicity, scalability and cost effectiveness. In the history of research on water splitting photocatalysis, perovskites and their derivatives have occupied a prominent position among hundreds of semiconductor photocatalysts studied to date. Shortly after the milestone discovery of TiO_2 photoelectrochemistry for water splitting, successful hydrogen liberation from water using $SrTiO_3$ as a photocatalyst ignited the enthusiasm for perovskite photocatalysis [1]. In 2003, readers witnessed a benchmark report on La doped $NaTaO_3$ with apparent quantum yield as high as 56% at 270 nm for water splitting [2]. This record was not broken until lately on Al doped $SrTiO_3$ that approached 69% at 365 nm [3]. The prosperity of this domain largely hinges on the flexibility of perovskite structure that is extremely tolerant to diverse cation/anion replacements, opening ample playgrounds in shaping and modifying the photocatalytic behaviour. Apart from single-absorber type photocatalysis, combining perovskite with other compounds as double-absorber type photocatalysts that mimic photosynthesis (Z-scheme) has also been successful in water splitting. Scalable water splitting from printable inks containing Rh doped $SrTiO_3$ and Mo doped $BiVO_4$ realize solar to hydrogen conversion efficiency of 1.1% (figure 2(a)) [4]. As most perovskite compounds are wide band gap semiconductors with little absorption to solar photons, exploring small band gap perovskites whose light absorption matches better with solar insolation has been the recent research focus. Typical examples include perovskite derivatives $LaMg_xTa_{1-x}O_{1+3x}N_{2-3x}$ ($x \geqslant 1/3$) and $Y_2Ti_2O_5S_2$ which are active for overall water splitting as far as 600 nm (figures 2(b) and (c)) [5, 6]. These studies have paved the way to the practical deployment of photocatalytic techniques to convert solar energy into hydrogen fuels.

1.2. Current and future challenges

Despite many promising aspects of perovskite photocatalysts, a solar to hydrogen efficiency (STH) of 10% for water splitting is needed to win commercial interest. This places very stringent standards on some fundamental steps during perovskite photocatalysis. The photocatalytic water splitting processes can be roughly divided into three basic steps: (a) photon absorption by photocatalyst to generated electron–hole pairs (η_a); (b) separation of electron–hole pairs and their migration to the surface reaction site (η_s); (c) participation of electrons and holes for water reduction and oxidation reactions at the surface (η_t). The overall efficiency for photocatalytic water splitting (η) therefore is determined by these three steps, i.e. $\eta = \eta_a \times \eta_s \times \eta_t$. Optimizing each step is indispensable to achieve a high overall efficiency. Since solar insolation is dominated by photons in the visible light region, development of photocatalytic water splitting using visible light photons is the premier target. This is mainly challenged by the reduced energetics of electrons and holes generated by visible light photons. For instance, generation of electron–hole pairs by photon excitation in semiconductors occurs generally in femtosecond (10^{-15} s) while water reduction and oxidation reactions driven by charges with low potential can take milliseconds to seconds (10^{-3} s $\sim 10^{\circ}$s). Such a huge difference in timescale between charge generation and charge consumption indicates the importance of charge separation step upon which a long lifetime has to be maintained for photo-generated charges. Pursing strategies that are effective for charge separation is the key toward visible light photocatalytic water splitting on perovskites. Another challenge that needs to be solved is the development of non-noble metal based co-catalysts which not only reduce the energy barriers for water splitting but also remain inert to back reactions of the products. This can be rationalized by the slow water oxidation half-reactions which involve four protons and four holes, being of both thermodynamic and kinetic difficulties.

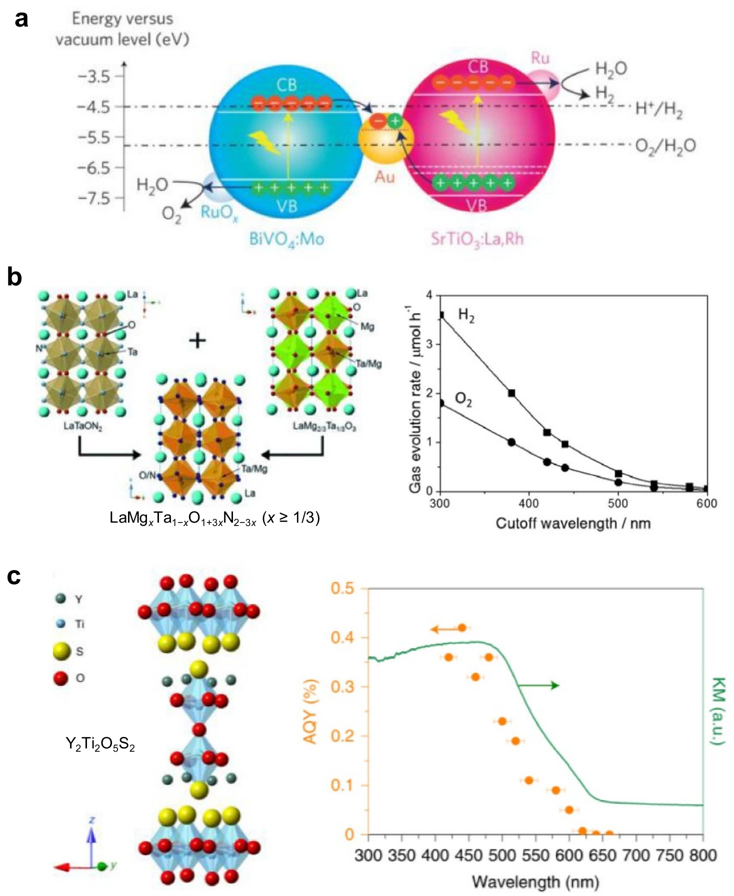

Figure 2. (a) Schematic of overall water splitting on the Ru-modified SrTiO3:La, Rh/Au/BiVO4:Mo sheet. CB, conduction band; VB, valence band [4]. Reprinted by permission from Springer Nature Customer Service Centre GmbH: Nature, Nature Materials [4] © 2016. (b) Crystal structures of $LaMg_xTa_{1-x}O_{1+3x}N_{2-3x}$ ($x = 0$–2/3) and the dependence of H_2 and O_2 evolution rate from pure water over $TiOXH/SiOXH/RhCrO_y/LaMg_{1/3}Ta_{2/3}O_2N$ on cutoff wavelength of incident light [5]. Reprinted by permission from Springer Nature Customer Service Centre GmbH: Nature, Nature Materials [5] © 2019. (c) Crystal structure of $Y_2Ti_2O_5S_2$ and overall water splitting using $Cr_2O_3/Rh/IrO_2$-modified $Y_2Ti_2O_5S_2$ on incident light wavelength, along with diffuse reflectance spectra of $Y_2Ti_2O_5S_2$ for comparison (green line); AQY, apparent quantum yield; KM, Kubelka-Munk transformations [6]. [6] John Wiley & Sons. © 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

1.3. Advances in science and technology to meet challenges

Although challenges remain for perovskite solar water splitting, advances in new perovskite materials or photocatalytic mechanisms might be a breakthrough. This has been seen in some perovskite systems where fundamental steps for photocatalytic water splitting can be significantly facilitated. For instance, new metallic oxide photocatalysts Sr_xNbO_3 ($0.8 \leqslant x \leqslant 0.9$) with light absorption threshold around 1.8 eV have water splitting activity under visible light illumination (figures 3(a) and (b)) [7]. The lack of energy gap for these metallic oxides indicates a new mechanism for photocatalytic water splitting. The high dielectric environment of perovskite Sr_xNbO_3 significantly red shifts the plasmonic frequency of free *d* electrons, contributing to hot electron generation under visible light illumination which participate in water splitting reactions. In this case, energetic electrons are generated by visible light photons that are highly reactive for water splitting. Another example is ferroelectricity assisted charge separation in $PbTiO_3$ [8, 9]. The degeneration field in single domain $PbTiO_3$ can induce effective separation of photogenerated electron–hole pairs as evidenced by the selective distribution of the reductive and oxidative deposits (figure 3(c)), and the selective deposition of the co-catalyst Pt on the positively poled (00-1) of $PbTiO_3$ led to a great enhancement in photocatalytic hydrogen evolution compared with the random deposition of Pt on both (001) and (00-1) surfaces [8]. To overcome the restraint of a large Schottky barrier between Pt and $PbTiO_3$ in transferring photogenerated electrons, the selective growth of epitaxial anatase (001) TiO_2 islands on the positively poled (00-1) surface was realized to further separate photogenerated charges and thus improve photocatalytic water splitting activity (figure 3(d)) [10]. As perovskites are known for their special properties such as dielectric, ferroelectricity, piezoelectricity, colossal magnetoresistivity, superconductivity and phosphorescence etc, coupling these properties with some fundamental steps of photocatalysis may lead to considerable enhancements on water splitting efficiency. Besides, massive research efforts on hydrogen

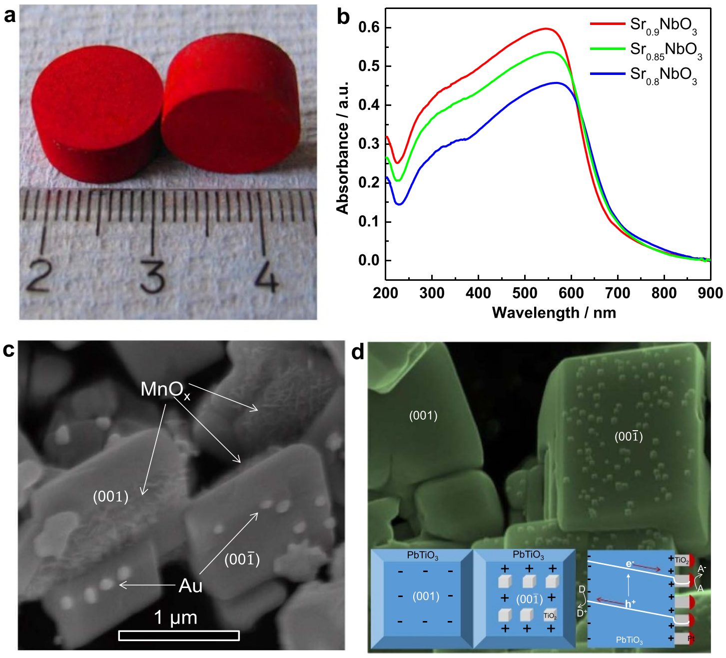

Figure 3. (a) Typical sintered pellets ($Sr_{0:9}NbO_3$) and (b) ultraviolet–visible absorbance spectra (converted from diffuse reflectance spectra) for $Sr_{1-x}NbO_3$ ($x = 0.1$, 0.15 and 0.2) [7]. Reprinted by permission from Springer Nature Customer Service Centre GmbH: Nature, Nature Materials [7] © 2012. (c) SEM image of the $PbTiO_3$ nanoplates with simultaneously photo-deposited MnO_x and Au nanoparticles on two opposite sides of the nanoplates [8]. Reproduced from [8] with permission of The Royal Society of Chemistry. (d) SEM image of the $PbTiO_3$ nanoplates with negatively poled (001) and positively poled (00-1) surface exposed. The inset shows the separation of photogenerated electrons and holes in $TiO_2/PbTiO_3$ [10]. Reprinted from [10], Copyright (2018), with permission from Elsevier.

evolution reaction and oxygen evolution reaction catalyst have shown some encouraging results on non-noble metal based catalysts that are highly active for water splitting under neutral pH.

1.4. Concluding remarks

Photocatalytic water splitting has been actively pursued during past half century and witnessed a number of perovskites or perovskite systems as promising photocatalysts for water splitting reactions. The continuous breakthroughs on water splitting efficiency of perovskite based photocatalysts enriches the possibilities of practical deployment for this tempting technique. Nevertheless, challenges still remain. The need to develop stable visible-light-active perovskites for water splitting places stringent standards on every fundamental step of photocatalysis. In particular, how to efficiently separate photo-generated electron–hole pairs and construct facile charge transfer pathways at perovskite surface are the main issues to be solved. However, opportunities exist in the development of new perovskite photocatalysts as well as new photocatalytic mechanisms. The structural and compositional diversities of perovskite compounds and their peculiar physicochemical properties can excavate to have great potentialities in tailoring their photocatalytic performance. With continuous efforts devoted to this field, the benchmark STH of 10% is likely to be achieved in the foreseeable future.

Acknowledgments

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2. Solar-driven thermochemical fuel production

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2.1. Status

Recent dramatic cost reductions in solar and wind energy technologies have turned the spotlight on energy storage as the missing link in the bridge to a sustainable energy future. Two-step solar thermochemical hydrogen (STCH) production has emerged as an attractive route for meeting the storage demand. The process is conceptually rather simple. A metal oxide is reduced at a high temperature, and then in a second, water splitting step, typically at a lower temperature, the reduced product is allowed to react with steam. In this step oxygen from the H_2O molecules are incorporated into the oxide, resulting in the generation of hydrogen.

Like many ideas in energy storage and conversion, thermochemical hydrogen production has a long history. A variety of multi-step cycles have been pursued, each with its own strengths and weaknesses. Two-step STCH employs the smallest number of steps possible—even direct thermolysis is more complex—and as such offers the promise of simplicity in system design. Interest in this approach has been driven in recent years by the recognition that non-stoichiometric oxides, which gently 'exhale' oxygen upon reduction and 'inhale' it during water splitting, offer advantages over previous stoichiometric approaches in terms of overall reaction kinetics and the robustness of the oxide structures to the cycling process [11].

Early efforts in the use of nonstoichiometric oxides employed ceria and doped derivatives [11]. The high temperature required for inducing a non-negligible release of oxygen from these fluorite-structured materials was quickly recognized as a drawback [12]. Furthermore, because only few variable-valence cations are large enough to accommodate the 8-fold oxygen coordination of the fluorite structure, opportunities for overcoming the temperature challenge through chemical modifications appear to have been exhausted. Inorganic perovskite oxides, in contrast, with two distinct cation sites, can accommodate a large majority of the elements of the periodic table. Thus, the perovskites have become the new frontier in the search for improved STCH materials [13, 14].

2.2. Current and future challenges

The vast chemical space encompassed by perovskites creates both opportunities and challenges in the design of STCH materials. As a first step towards navigating this space, it is essential to understand the reactions involved in the thermochemical process. The thermal reduction and water splitting reactions for the explicit case of $ABO_{3-\delta}$ perovskites, where δ is the oxygen non-stoichiometry, are presented in equations (1) and (2), respectively:

$$\text{Temperature} = T_R \frac{1}{\Delta\delta} ABO_{3-\delta_i} \rightarrow \frac{1}{\Delta\delta} ABO_{3-\delta_f} + \frac{1}{2} O_2 \tag{1}$$

$$\text{Temperature} = T_{WS} \frac{1}{\Delta\delta} ABO_{3-\delta_f} + H_2O \rightarrow \frac{1}{\Delta\delta} ABO_{3-\delta_i} + H_2. \tag{2}$$

Here $\Delta\delta = \delta_f - \delta_i$ is defined as the change in oxygen content between the initial and final values of oxygen non-stoichiometry that occur in the reduction step, and T_R and T_{WS} are the respective temperatures at which reduction and water splitting are carried out. As written we assume that the cycling is chemically closed such that the non-stoichiometry at the completion of the reduction half-cycle corresponds to that at the initiation of the water splitting half-cycle, and vice versa. In the limit $\Delta\delta \rightarrow 0$, the standard Gibbs energy of the reduction reaction is given by

$$\Delta_{red} G^{\phi}(T, \delta) = -RT \ln(K_{red}^{eq}) = -RT \ln(\hat{p}O_2)^{1/2} = \Delta_{red} H^{\phi}(\delta) - T\Delta_{red} S^{\phi}(\delta) \tag{3}$$

where K_{red}^{eq} is the equilibrium reduction constant, $\hat{p}O_2$ is the (unitless) oxygen partial pressure referenced to the reference state of 1 atm, and $\Delta_{red} H^{\phi}(\delta)$ and $\Delta_{red} S^{\phi}(\delta)$ are the standard enthalpy and standard entropy of reduction, respectively.

A key goal in STCH research is to develop materials for which both reduction and water splitting are favourable. As these two reactions are not thermodynamically independent, the material properties demands translate into overall requirements that the enthalpy of the reduction reaction be 'moderate' and, presuming that water splitting is carried out at a temperature lower than reduction, that the corresponding entropy be as large as possible [15].

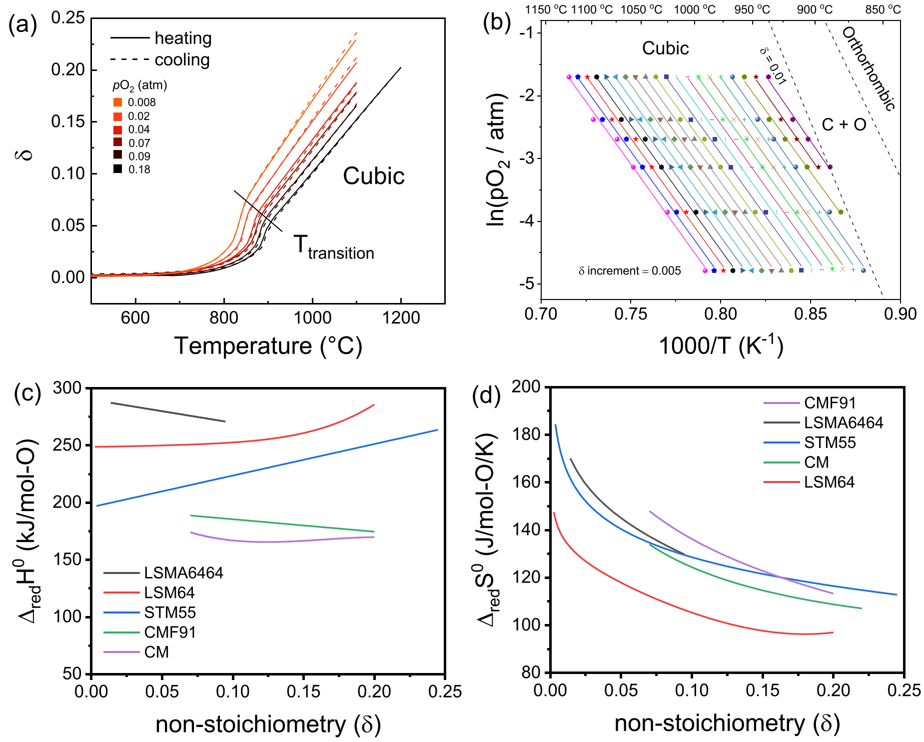

Figure 4. Redox thermodynamics in representative oxide perovskites: (a) non-stoichiometry as a function of temperature and oxygen partial pressure in $CaMnO_{3-\delta}$ as determined by thermogravimetric analysis; (b) Arrhenius representation of iso-stoichiometric T and pO_2 conditions determined from (a); (c), (d) enthalpy and entropy of reduction, respectively, in $La_{0.6}Sr_{0.4}Mn_{0.6}Al_{0.4}O_{3-\delta}$ [18], $La_{0.6}Sr_{0.4}MnO_{3-\delta}$ [19], $SrTi_{0.5}Mn_{0.5}O_{3-\delta}$ [20], $CaMnO_{3-\delta}$ [16] and $CaMn_{0.9}Fe_{0.1}O_{2.95-\delta}$ [16]. In (b) the exceedingly narrow phase field of the tetragonal phase is omitted for clarity.

2.3. Advances in science and technology to meet challenges

The redox thermodynamics of oxides are most easily determined from thermogravimetric measurements or coulometric titrations under controlled temperature and oxygen partial pressure conditions. Following the van't Hoff approach, the set of oxygen partial pressure values and corresponding temperatures that give rise to a given δ is plotted in Arrhenius form, and the slope and intercept yield the enthalpy and entropy, respectively. An example of such an analysis is shown in figure 4 for the perovskite $CaMnO_{3-\delta}$ [16], which crystallizes with an orthorhombic distortion at ambient conditions ($GdFeO_3$ structure type) and transforms to an oxygen deficient cubic form above ~920 °C in air.

One can immediately surmise that if the thermodynamic properties are well known, then the equilibrium hydrogen production capacity of any given material, for any pair of states in the reduction and water splitting half-cycles, can be computed. What is less obvious is that the thermodynamic properties also strongly influence the rate at which fuel is produced. Consider a material for which the bulk diffusion of oxygen and the surface reaction rate are exceptionally large. In such case, it is reasonable to expect that the macroscopic rate at which the solid reacts with the gas phase will be limited by how quickly the gas is supplied. That is, if the material kinetic parameters are sufficiently large, the solid will immediately equilibrate with the gas such that the driving force for further reaction is nil until the next incremental unit of gas is supplied. If the volume of the porous material is furthermore sufficiently small that the gas enveloping it is uniform in composition and the reactor is designed such that thermal gradients across the sample are negligible, then the rate of change in oxygen stoichiometry are given by straight-forward mass balance considerations. The expressions for the reduction and water splitting steps are respectively [17]

$$\frac{\mathrm{d}\delta_{\mathrm{red}}}{\mathrm{d}t} = 2\bar{F}_{\mathrm{TR}}\frac{\left(pO_2(\delta, T_{\mathrm{TR}}) - pO_2^{\mathrm{TR}}\right)}{\left(p_{\mathrm{tot}} - pO_2(\delta, T_{\mathrm{TR}})\right)} \tag{4}$$

and

$$\frac{\mathrm{d}\delta_{\mathrm{ox}}}{\mathrm{d}t} = \bar{F}_{\mathrm{WS}}\frac{\left(2pO_2(\delta, T_{\mathrm{WS}}) - \psi\chi_{\mathrm{H_2O}}\left(p_{\mathrm{tot}} - pO_2(\delta, T_{\mathrm{WS}})\right)\right)}{\left(p_{\mathrm{tot}} - pO_2(\delta, T_{\mathrm{WS}})\right)} \tag{5}$$

with the reaction extent given as, $\psi = \frac{K_{\mathrm{H_2O}}(T_{\mathrm{WS}})}{\hat{p}_{O_2}^{1/2} + K_{\mathrm{H_2O}}(T_{\mathrm{WS}})}$.

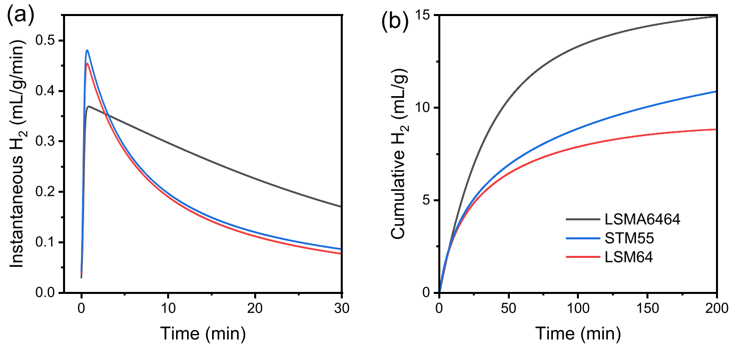

Figure 5. Computed hydrogen production profiles for $La_{0.6}Sr_{0.4}Mn_{0.6}Al_{0.4}O_{3-\delta}$ (LSMA6464) $La_{0.6}Sr_{0.4}MnO_{3-\delta}$ (LSM64), and $SrTi_{0.5}Mn_{0.5}O_{3-\delta}$ (STM55) for conditions specified in the text: (a) instantaneous hydrogen evolution at short times, and (b) cumulative hydrogen production.

Here $\bar{F}_{TR}$ and $\bar{F}_{WS}$ are the molar flow rates of the gas in thermal reduction step and water splitting steps, respectively, normalized by the moles of oxide (mol gas/time/mol oxide), pO_2^{TR} is the oxygen partial pressure of the supplied reduction gas, χ_{H_2O} is the fraction of steam in the gas supplied in the water splitting step, K_{H_2O} is the equilibrium thermolysis reaction constant, p_{tot} is the total pressure (typically 1 atm), and $pO_2(\delta,T)$ describes the relationship between the instantaneous pO_2 and δ at the reaction temperature as given in equation (3). Beyond revealing that gas production profiles can be directly computed from thermodynamic behaviour (providing the experimental conditions described are met), equations (4) and (5) show that the rate of hydrogen production can be readily manipulated by changing the gas flow rates or quantity of oxide in the reactor.

Despite the profound importance of the thermodynamic terms of equation (1), the values have been reported for only a limited number of perovskites. A set of representative examples accompany the results presented in figure 4 for $CaMnO_3$. The raw data from the original sources are represented by fitted functions to ease calculations of the profiles according to equations (4) and (5). The fitting is constrained only by the recognition that the entropy, which includes the configurational entropy of the solid, must contain a term proportional to $-\ln(\delta)$. The materials selected, $La_{0.6}Sr_{0.4}Mn_{0.6}Al_{0.4}O_{3-\delta}$, $La_{0.6}Sr_{0.4}Mn0_{3-\delta}$ and $SrTi_{0.5}Mn_{0.5}O_{3-\delta}$, are ones that have recently been shown to have promising hydrogen production capacity, or in the case of $CaMnO_{3-\delta}$ and $CaMn_{0.9}Fe_{0.1}O_{2.95-\delta}$, promising heat storage capacity.

Representative computed hydrogen production profiles, figure 5, demonstrate the extreme impact of the thermodynamic properties on the apparent kinetic response. The calculations are done for the following set of conditions: 0.5 g of material, oxygen partial pressure in the gas stream of the preceding reduction step of 10^{-5} atm, reduction temperature of 1400 °C, reduction gas flow rate of 500 ml min^{-1}, reduction time of 30 min, water splitting at 1000 °C, steam partial pressure in the oxidation gas stream of 0.4 atm, oxidation gas flow rate of 250 ml min^{-1}. The $CaMnO_{3-\delta}$ and $CaMn_{0.9}Fe_{0.1}O_{2.95-\delta}$ materials are omitted from the results because these materials, with relatively low enthalpies of reduction, are not amenable to oxidation by steam at pressures below 1 atm. The data immediately reveal that hydrogen evolution is very sluggish for all three of the materials treated. The apparent kinetic limitation is most severe for $La_{0.6}Sr_{0.4}Mn_{0.6}Al_{0.4}O_{3-\delta}$, although beyond an oxidation time of 6–7 min this material produces more hydrogen than the others. A similar calculation for ceria reveals a thermo-kinetic profile in which hydrogen production is essentially complete within 2–3 min [19], in stark contrast to the hours-long timescale for the perovskites to approach reaction completion.

It is to be emphasized that the behaviour illustrated in figure 5 is entirely divorced from what might be considered 'true' material kinetic properties: the surface reaction rate and the oxygen diffusivity of the solid. Of course, if the kinetic parameters are unfavourable, they will induce an additional penalty on the rate. Or viewed from a different angle, if the gas is supplied at a sufficiently high rate relative to the oxide mass, material kinetics will become rate-limiting. Experience with both perovskites and fluorites indicates that when material kinetic factors do become important, it is the surface reaction step rather than bulk diffusion that is rate-limiting [19], not surprising given the relatively short (<100 μm) diffusion distances in porous oxides used for STCH applications. Though not a solved problem, a variety of surface engineering tools abound for enhancing surface reaction rates. Thus, the challenge for STCH materials development returns to the problem of manipulating the reduction thermodynamics.

2.4. Concluding remarks

The analysis presented here underscores the overwhelming significance of the thermodynamic properties of oxide perovskites for solar-thermal hydrogen production. In recent years, computational design of materials has garnered a great deal of attention, and the prospects for *ab initio* prediction of reduction energies appear high [13, 15]. Computational prediction of entropy, on the other hand, remains tenuous, particularly for materials such as $LaMnO_{3-\delta}$ and $CaMnO_{3-\delta}$ that have ground states that differ structurally from the phases relevant to high temperature thermochemical cycling. Yet entropy is arguably more relevant than enthalpy for enhancing STCH performance in two-temperature cycles. Accordingly, it is likely that experiment and computation will go hand in hand in the effort to identify sources of entropy that go beyond the configurational and vibrational sources that dominate today's STCH perovskite candidates.

Acknowledgments

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3. Thermoelectric energy conversion

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3.1. Status

The underlying principles of the thermoelectric (TE) effects have been known for almost 200 years, but practical exploitation has been limited to the last few decades; NASA, for example, has used thermoelectric generators (TEGs) in space missions since 1961 [21]. TEGs offer long term, direct conversion of heat to electricity without high maintenance costs, but with the advantage of scalability. However, traditional TE materials, e.g. Bi_2Te_3, PbTe and SiGe suffer from low abundance of the constituent elements, toxicity or high cost. Additionally, their conversion efficiency is temperature dependent and they have a narrow temperature range of operation. These limitations, and increasing environmental concerns in the 1990s, stimulated activity in oxide TEs [22]; they offer high temperature stability, lower weight, and are more environmentally-friendly. Oxide based perovskites have emerged as the most promising n-type oxide TEs; the flexible nature of perovskite structure provides many options for tuning the transport properties.

Candidate materials are usually evaluated in terms of the TE figure of merit ZT ($ZT = \sigma S^2 T/\kappa$, where T is absolute temperature, σ is electrical conductivity, S is the Seebeck coefficient and κ is thermal conductivity); ZT needs to be maximised. The TE inorganic oxide perovskites include $SrTiO_3$, $CaMnO_3$ and A-site deficient lanthanides such as $Ln_{2/3}TiO_3$ (Ln = La, Pr, Nd etc). Typical strategies for improving ZT of these materials (figure 6) are single or dual donor doping on A- and/or B-sites, generating A-site cation vacancies or oxygen deficiency, and optimising processing conditions [23]. Selection of appropriate dopants at an optimised level can increase the electronic performance (namely the power factor $PF = \sigma S^2$) and also reduces thermal conductivity.

Although oxide perovskites exhibit modest ZT values ($\leqslant 0.5$), lower than current commercial TE materials ($ZT \sim 1.0$), the high PF values of the oxides (comparable to that of Bi_2Te_3) and the tunability of κ (figure 6) indicates their promise for high temperature TE applications. The growing understanding of these material systems and predictions based on modelling studies suggests there is considerable scope for improvement in the ZT values by grain boundary (GB) engineering [24], combined with a wide operational range of temperature.

3.2. Current and future challenges

The main limitation of inorganic perovskites for TE applications is the low ZT values. This arises from either low PF (σ and/or S) or high thermal conductivity (κ); the latter is the limiting factor for $SrTiO_3$ based TE materials while $CaMnO_3$ based materials suffer from both problems. Thus, the primary challenges are to increase σ and reduce κ, which are directly linked.

In order to increase σ, donor doping on the perovskite A, B or A + B sites is typically undertaken (figure 7) to increase the carrier concentration (n). However, the dependency of the Seebeck coefficient on n requires the doping concentration to be optimized; the low carrier mobility (μ) for perovskite oxides means that relatively high carrier concentrations (10^{20}–10^{21} cm^{-3}) may be needed to maximize the PF [25]. Moreover, the limited solubility of the dopants restricts the level of doping that can be utilized. Another approach is to adjust the degree of oxygen deficiency and the microstructure of the materials through control of processing route (figure 7). An increase in oxygen deficiency provides additional carriers, which increases PF. However, high levels of oxygen deficiency may limit the maximum operating temperature of the materials [26]. Conversely, there are opportunities through combinations of processing techniques to design microstructures such as core–shell type grains, nanostructures with nanoporosity and novel GB characteristics, to enhance the electronic transport properties [23]. The high thermal conductivity κ of the inorganic perovskites is linked to the relatively simple crystal structure and the presence of light elements.

Strategies to reduce κ have often been based on the introduction of phonon scattering centres, e.g. heavy atoms or structural defects. Layered structured compounds, such as A-site deficient perovskites [23], offer inherent benefits of low κ in directions. For oxides such as $SrTiO_3$, the mean free path of phonons (l_{ph}) is quite small, <10 nm. This requires the presence of atomic scale defects (typically oxygen and A-site cation vacancies) for the reduction of thermal conductivity. In general oxygen vacancies are beneficial for optimising both electronic and thermal transport. However, A-site vacancy concentrations need to be carefully adjusted for effective reduction of κ without degrading electrical conductivity.

3.3. Advances in science and technology to meet challenges

As noted above the main challenges for TE inorganic oxides are to develop ways to overcome the inherent limitations of low electrical conductivity and high thermal conductivity, and to decouple the two transport

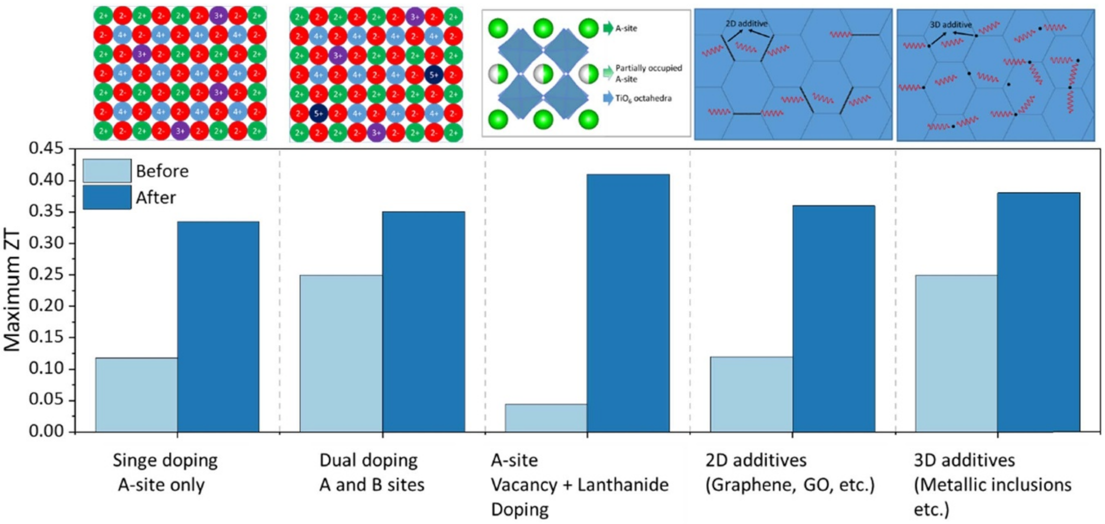

Figure 6. Current strategies employed for the improvement of the thermoelectric properties of inorganic oxide perovskites [23]; (i) single element doping on A-site, (ii) dual doping on A- and B- sites, (iii) combined vacancy and lanthanide doping on A-site, (iv) embedding 2D additives, such as graphene, into oxide perovskite matrix and (v) incorporation of 3D additives, i.e. metallic inclusions, into the matrix. For the single and dual element doping figures, A-site (2+ valance) cation, B-site (4+ valance) cation and oxygen atom (2− valance) are represented by green, light blue, and red circles, respectively; donor doping on A-site with 3+ valance and B-site with 5+ valence cations are shown by purple and dark blue circles, respectively. In the schematic microstructure figures (top right-hand side) the red springs represent the movement of phonons within the material. The darker coloured bars represent the dimensionless figure of merit, ZT of thermoelectric perovskite oxides after strategies listed are utilized.

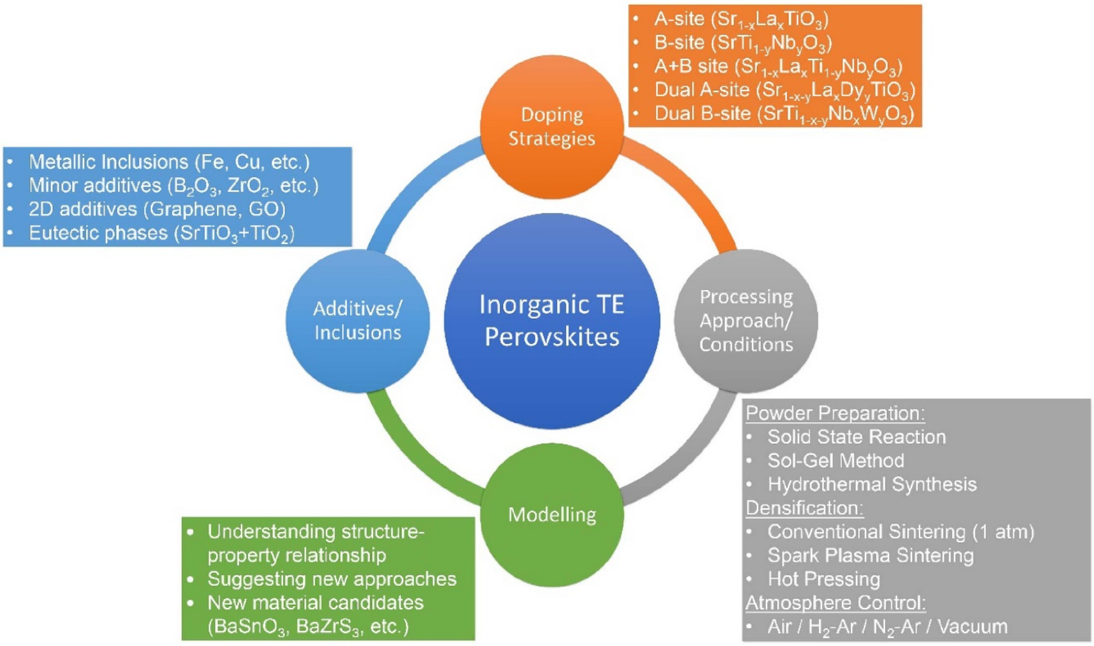

Figure 7. Summary of the research approaches for the developments of inorganic perovskites for thermoelectric applications.

processes. Advances in processing technologies allow the preparation of materials with nanostructures containing high concentrations of phonon scattering centres, which yields perovskites with thermal conductivities close to the theoretical minimum [27]. The real breakthrough will come when we have materials with both low thermal conductivity and high electrical conductivity and therefore high ZT (ideally above 1.0) over a wide temperature range, since high average ZT is much more valuable than peak ZT. Recent work on composites involving the incorporation of two dimensional additives in perovskite oxides, enabling simultaneous improvement in PF and reduction in κ over a range of several hundred degrees [28] is very promising. Furthermore, new models suggest that suppression of GB resistance by utilising 2D additives could lead to ZT > 0.7 over a wide temperature range in perovskite oxides [24]. A better understanding of grain boundaries and routes to fabricate materials with optimized defect structures are essential if oxides are to reach their full potential.

Another aspect of TE inorganic perovskites which is ripe for development is the discovery of new candidate materials by computational modelling (figure 7). Groups of potential candidates could be identified and screened before commencing detailed experimental investigations. Recent work on sulphide based inorganic perovskites and the observation of low κ in $BaZrS_3$ [29] suggest that these materials could be promising candidates for TE power generation; however, our understanding of the transport properties of these sulphides is at an early stage. Finally, there is increasing evidence that ZT values reaching unity can be achieved for a range of inorganic perovskites including oxides, chalcogenides [29] and stannates (e.g. $BaSnO_3$) [30]. With tailored fabrication techniques and improvement the understanding structure-property relationship of these inorganic perovskites there could be significant improvements in their transport properties.

3.4. Concluding remarks

As clean energy sources gain increasing importance it is clear that TEs can make a valuable contribution in many industrial sectors and indeed domestic environments. Exploitation of TEs, in generating power from waste heat, has so far been quite modest, mainly because of high cost and the limited temperature range of operation. Inorganic perovskites offer much in terms of lower weight and cost than traditional TEs, environmental advantages, a much wider temperature operational window and potentially higher average ZT. Further developments in processing methods and modelling work to define both new candidate materials and optimized micro-nanostructures to give the desired enhanced thermal and electrical transport performance are urgently needed to allow the inorganic perovskites to reach their full TE potential. The understanding of interfaces and the desired tuning of electrical and thermal conductivity will be a key aspect of achieving the breakthrough.

Acknowledgments

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4. Inorganic perovskite oxides for solid oxide air electrodes

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4.1. Status

Offering tremendous flexibility to design the physical and chemical properties of materials, inorganic perovskite oxides of the general formula $ABO_{3-\delta}$ are central to the design of air electrodes for solid oxide cells (SOC). The composition can be tailored to obtain a large number of compounds through partial or total substitution of one or more cations at both the A- and B-sites [31]. While new compositions with enhanced properties continue to be explored, substantial efforts are also made to understand the reaction mechanisms at interfaces, microstructural effects and long-term degradation issues.

In terms of electrode designs, an exciting development in the field came with the concept of interface engineering. With advances in thin film technologies such as pulsed laser deposition (PLD) and atomic layer deposition (ALD), interfacial designs have reached new heights. By controlling the strain, which originates from the lattice mismatch between the thin film and the substrate, it was shown that oxygen non-stoichiometry, surface chemistry and charge-transfer kinetics could be significantly modified. In this way, orders of magnitude faster ion-diffusion kinetics were obtained [32, 33]. Studies have also shown increased catalytic activity at the heterointerface of two inorganic perovskite-related oxides, both in the porous electrode microstructure and in the strained thin films [34] as illustrated schematically in figure 8. Microstructural optimisation such as reducing particle sizes to the nanometre length scale, and surface decoration by infiltration techniques to improve catalytic activity and the durability, have become common routes in the design of SOC air electrodes.

The fact that SOC technology can be used reversibly for both energy and fuel production is increasing its importance [35]. Power-to-X (X, e.g. fuel) applications are expected to play a significant role in addressing the utilisation of surplus renewably generated power. Here, we focus on the current goals and challenges of developing inorganic perovskites for air electrodes in this sector and discuss future developments in the science and technology needed to overcome the challenges associated with large scale deployment of these devices.

4.2. Current and future challenges

Despite many advantages such as high efficiency and fuel flexibility, SOC systems are mainly considered for stationary applications. For this technology to break into commercial markets, the application areas of these devices should expand towards portability and reversible usability. The current challenges of implementing the technology in portable applications arises from the low efficiency of existing materials at low temperatures and the lack of current technology for miniaturisation. This is a particular challenge in the area of multicomponent oxide ceramics where production of devices relies on advanced deposition techniques (PLD, ALD). Preparation of arrays of solid solution series by PLD is possible, but these are typically at research laboratory level with the aim of identifying new high performance perovskite compositions. This leads to a further challenge in the effective screening of materials properties (ionic transport, catalytic activity etc).

A further issue is the scalability of these new devices. Interesting and exciting results continue to be shown at the single-cell scale in laboratories; however, questions remain whether similar performance can be obtained at large scale both in terms of cost and applicability. It will take more time to encourage existing commercial entities to adopt next-generation materials and incorporate them into their product ranges. Future research should focus on the integration of our existing knowledge in nanotechnology, developed for electronics, to ceramic materials. Increased collaboration between the fields of solid-state ionics and other nanotechnology communities is essential.

In terms of reversible use, studies continue to investigate whether or not the same electrode materials can efficiently work in power-to-fuel and fuel-to-power operations over an extended period. As mentioned previously, reduced operating temperatures offers several advantages in terms of long-term operation, lower elemental interdiffusion between layers and more options for chemically-stable materials [36].

4.3. Advances in science and technology to meet challenges

To move towards effective low temperature devices high performance air electrodes based on the perovskite framework are required. Single perovskites of composition ABO_3 have proven effective in conventional devices, but as requirements shift to lower temperatures of operation, materials with higher catalytic activity, higher ionic and higher electronic conductivity are necessary.

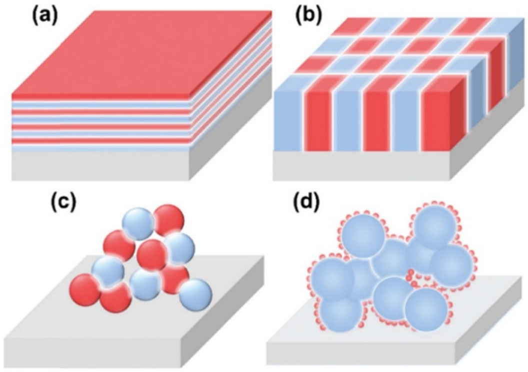

Figure 8. Schematic representation of different heterostructures (a) multilayers, (b) vertically aligned nanocomposite, (c) composite structure and (d) infiltrated porous structure. Reproduced from [34] with permission of The Royal Society of Chemistry.

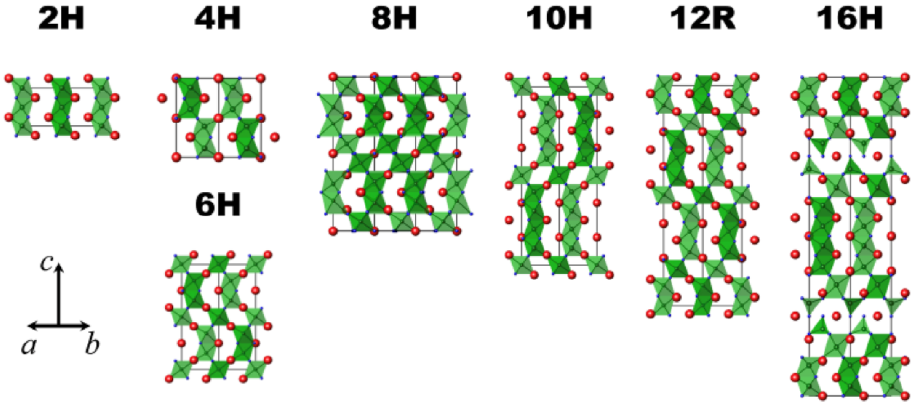

Figure 9. Schematic representation of the series of hexagonal perovskites as discussed as potential new air electrode materials. Reproduced from [38]. © IOP Publishing Ltd. CC BY 3.0.

In terms of the materials developments it is essential that new materials are identified, and this may include a wide range of perovskite-related compositions. Double perovskites of formula AA'BB'O_{6-d}, layered perovskites ($A_{n+1}B_nO_{3n+1}$) [37], $BaNdInO_4$-type and more recently hexagonal perovskites, figure 9, with compositions of $Ba_3NbMO_{8.5}$ and $Ba_7Nb_4MoO_{20}$ have been proposed as materials that have excellent ionic conductivity at low temperatures, both oxide ion and protonic [38]. To date there has been little optimisation of the mixed conducting properties of these classes of materials, but they do highlight the drive to develop new Sr free materials as a route to prevent surface segregation and thus degradation of performance.

In developing these new inorganic perovskites, it is clear that there is also a drive to produce compositions that exhibit a combination of oxide ion, proton and electronic species, with optimum mobility for all three species at low temperatures (300 °C–400 °C). Unambiguously distinguishing these charge carrying species has proven demanding but would prove extremely beneficial for development of SOC electrodes, particularly in the area of electrolysis.

One further route with great potential that has yet to be explored is the field of high entropy oxides [39, 40]. In these materials multicomponent compositions are found to entropically stabilize oxides and provide enhanced physical properties, and have already been reported in the field of ion conductors. This nascent field offers considerable opportunity to develop novel high-performance ceramics for low temperature operation and may find application in thin film devices.

4.4. Concluding remarks

Research on SOC air electrodes has revealed well-understood reaction mechanisms and factors affecting catalytic activity from the atomic to micro-scale. Engineering of defect structures at surfaces and (hetero-)interfaces will continue to lead the design of improved electrodes at reduced temperatures. Transforming these research concepts into a technologically viable design will provide opportunities for significantly improved air electrodes.

On the other hand, the field is going to expand towards reversible power-to-fuel and fuel-to-power applications at reduced temperatures. The increased desire to develop environmentally sustainable electrode compositions that do not contain rare-earth or carcinogenic elements will lead to the discovery of unconventional electrode compositions. Approaches such as high entropy materials development, combined with theoretical techniques such as molecular dynamics and density functional theory will advance materials discovery and optimisation of devices. Numerous opportunities for future development of inorganic air electrodes and an exciting research future await.

Acknowledgments

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5. Perovskite fuel electrode for solid oxide cell application

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5.1. Status

Materials with perovskite structure have been widely used in devices for energy generation, conversion and storage. Among these devices, solid oxide fuel cells (SOFCs) are important devices to convert chemical energy in hydrocarbons or other fuels into electricity at high efficiency. Solid oxide electrolysis cells (SOECs) can split steam into H_2 and O_2 for green H_2 production. The combination of SOFCs and SOECs enables a solid oxide to be operated in either SOFC or SOEC mode, which is called reversible SOFCs, having potential applications in renewable energy storage. SOFCs and SOECs are also classified as solid oxide cells (SOCs). SOECs can split CO_2 into CO and O_2 for CO_2 utilisation while valuable syngas can be produced through co-electrolysis of H_2O and CO_2. SOFCs can also be used for co-generation of electricity and valuable hydrocarbons to be used as chemical feedstock. The conventional anodes for SOFCs are metal-oxide cermets such as Ni-YSZ. The catalytic activity of Ni to the decomposing of CH_4 is so high that coking happens at the anode causing carbon deposition, blocking the anode pores. Volume change between NiO and Ni at the anode also causes delaminating of the anode/electrolyte interfaces, leading to cell degradation. Therefore it is desired to replace the cermet anode with materials able to tolerate redox changes without mechanical or electrochemical degradation. Particular focus has been on perovskite structures containing redox active mid-transition ions such as Mn, Fe, Mo. The first redox stable anode for SOFCs is the simple perovskite oxide $(La_{0.75}Sr_{0.25})Cr_{0.5}Mn_{0.5}O_{3-\delta}$ (LSCM) which exhibits comparable performance to the Ni-YSZ anode at high temperature [41]. Later on, it was found that La- and Mn-doped $SrTiO_3$, $La_4Sr_8Ti_{11}Mn_{0.5}Ga_{0.5}O_{37.5}$, also exhibits excellent redox property and performance when carefully engineered and used as anode for SOFCs [42]. B-site ordered double perovskite Sr_2FeNbO_6 was also investigated as potential anode for SOFCs but the conductivity is not high enough [43]. Double perovskite oxides $Sr_2MgMoO_{6-\delta}$ and $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ have been reported as good redox anodes for SOFCs [44, 45]. Layered oxygen deficient perovskite oxide $PrBaMn_2O_{5+\delta}$ was also found as a good anode for SOFCs [46]. To further increase the activity, oxides with exsolved metal particles on the surface exhibits excellent performance as anode for SOFCs [47]. For reversible SOFCs, oxides which are redox stable and exhibit high conductivity in both reducing and oxidising atmospheres, such as $SrFe_{0.8}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ are important for real applications of symmetrical SOCs [48]. These structure types are illustrated in figure 10.

5.2. Current and future challenges

Reversible SOFCs are ideal high temperature electrochemical devices which can be used in both SOFC and SOEC modes. The perovskite oxide LSCM is has been reported as the electrode in the first symmetric SOFC and also reversible SOFC [49]. A key requirement for symmetric reversible SOFCs is that, the electrode must exhibit high electronic conductivity in both anode (a strong reducing atmosphere) and cathode (a strong oxidising atmosphere) at high temperature. Among the redox stable oxides, some primitive perovskite oxides such as $SrFe_{0.9}Cu_{0.1}Nb_{0.1}O_{3-\delta}$ and double perovskite oxide $PrBaMn_2O_5$ exhibits reasonable conductivity in both reducing and oxidising atmospheres [46, 48]. However, the ionic conductivity of these redox perovskite oxides are normally not high enough to reduce the polarisation resistance at the electrodes. Therefore they are normally mixed with an electrolyte to form a composite electrode for enhanced ionic conductivity as well as matched thermal expansion coefficient (TEC) with the electrolyte to maintain good electrolyte/electrode interfaces. It is necessary to introduce suitable transition elements at the B-sites to improve the catalytic activity in order to reduce the polarisation resistance. Exsolving small metal particles on the surface of redox oxides is a promising strategy to improve the catalytic activity of the perovskite oxide electrodes when used as negative electrode and exposing in a reducing atmosphere [47, 50]. Cation segregation from the oxide electrode, may form unwanted non-conductive phases at the triple phase boundary (TPB). Therefore it is necessary to identify perovskite oxides which have sufficient catalytic activity for low polarisation resistance at reduced temperature in order to minimize the cation segregation. It is also required to reduce the sintering temperature of the electrolyte in order to co-fire electrode and electrolyte together. Infiltration of the perovskite can avoid high temperature firing but it is time-consuming and not always easily applied to fabrication of SOCs. When used for cogeneration or trigeneration, some special catalysts which can facilitate the reaction for desired product pathways should be incorporated into the composite electrodes or, exsolved after being exposed in a reducing atmosphere. Most redox stable perovskite oxides have good anti-coking properties when hydrocarbons are used as the fuels. However, the resistance to sulphur poisoning is not ideal

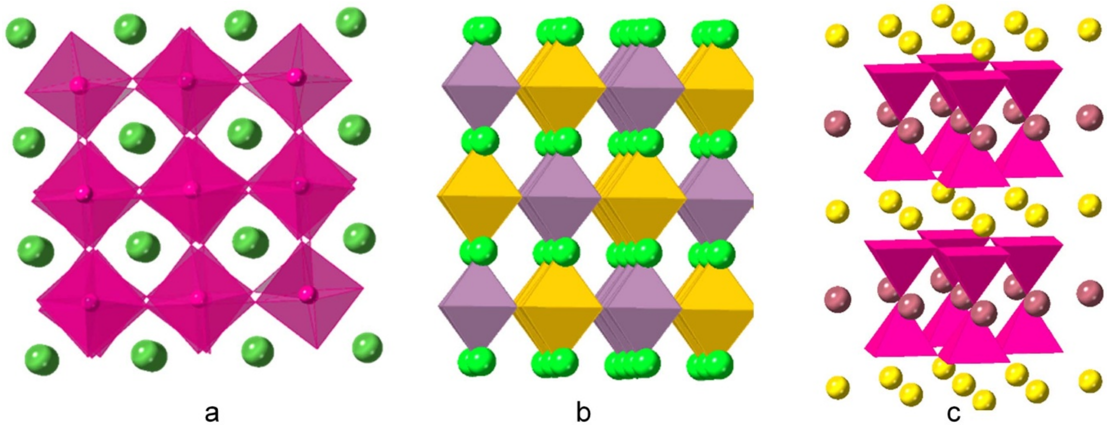

Figure 10. The crystal structure of some different candidate perovskite oxide fuel electrodes (a) B-site disordered $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$, (b) B-site ordered double perovskite $Sr_2MgMoO_{6-\delta}$, (c) layered $PrBaMn_2O_{5\pm\delta}$.

when high concentration of sulphur is included in the fuels. To develop new perovskite oxide negative electrode which can sustain higher level of sulphur containing compounds remains a big challenge.

5.3. Advances in science and technology to meet challenges

As a good perovskite anode for SOFC or cathode for SOEC, the fuel electrode must be redox stable in a strong reducing environment at high temperatures. Some primitive, double perovskite oxides and perovskite related oxides with Ruddlesden-Popper type layered structure have shown excellent redox stability. High electronic conductivity of these redox stable oxides in both reducing and oxidising atmospheres has been achieved in some oxides, mainly through doping at A and/or B-sizes. Introduction of multi-valent elements in the lattice normally improve the electronic conductivity and catalytic activity. The ionic conductivity of popular perovskite fuel electrodes from titanates, chromites to recently developed ferrites, should be enhanced to accelerate charge transfer over the electrodes and the interface between electrodes and electrolyte, and lower the polarization resistance of the whole cell. Materials with high ionic conductivity normally contain a large quantity of oxygen vacancies while the lattices of these oxides can be less stable, leading to poor stability in a reducing atmosphere. Doping to increase the concentration of oxygen vacancy or suppress oxygen vacancy ordering thereby introducing Sr and Y into the A site of titanate perovskite or transition metal (Mn, Fe, Co, Ni, Cu) into the B site of chromite and ferrite perovskite. The electrocatalytic activity can be significantly enhanced through the exsolution of nano-sized metal particles from the bulk [47]. Reducing the level of ordering of oxygen vacancies in Brownmillerite oxide such as $Sr_2Fe_2O_{5\pm\delta}$, making the oxygen vacancy mobile can also be a good strategy. In some specially designed oxides, nano-sized electronic conducting metal and ionic conducting oxide can be simultaneously exsolved, which is an ideal option. Under a reducing atmosphere, the exsolution process may take a long time. A new technology by applying a small DC voltage across the electrodes can shorten the exsolving process from hours/days to minutes, a big step forward for application of the exsolvation technology [47], figure 11. Unless methods for reducing the sintering temperature of existing electrolyte materials, co-sintering of perovskite oxide electrode and electrolyte can be difficult. Cation segregation from perovskite electrode can be reduced if the operating temperature of the SOCs can be reduced. Redox perovskite oxides which can tolerate some level of sulphur have been identified too. In general, after over 15 year development, negative electrodes based on redox stable perovskite oxides already meet the basic requirements for SOCs.

5.4. Concluding remarks

Redox stable perovskite oxides possess high electronic/ionic conductivity in both reducing and oxidising atmospheres, suitable TECs close to the electrolyte materials, good chemical compatibility with electrolyte and interconnector can be chosen as the ideal fuel electrodes for SOECs. Exsolving nano-particles from oxides with perovskite or perovskite related structure through reducing at high temperature or applying a voltage up to 2.3 V for just a few minutes, can significantly improve catalytic activity, reducing the polarisation resistance thus enhancing the performance of fuel cells and electrolysers. Due to their crystal structure, perovskite oxides (ABO_3) from titanates, chromites to ferrites are normally highly conductive, combining with the transition element dopants, which are widely used as fuel electrodes of SOCs. It is necessary to develop new perovskite oxides, which can be operated at reduced temperature to minimize the cation segregation and extend the stability. In order to reduce the SOCs' fabrication cost, co-sintering of the

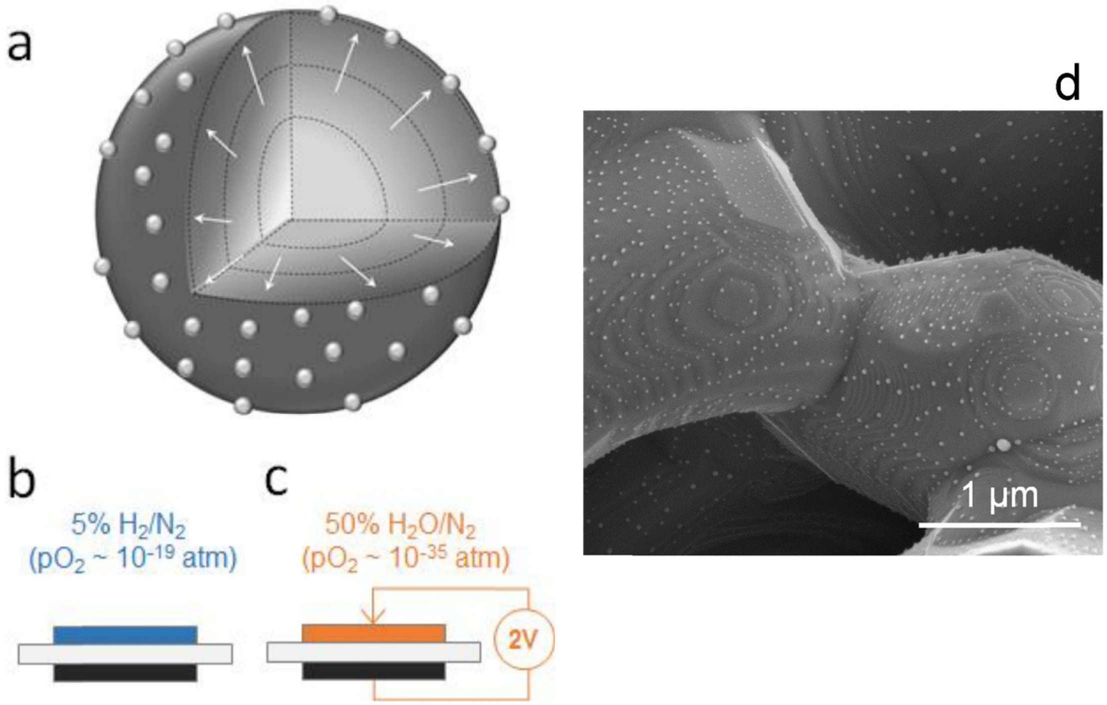

Figure 11. (a) Schematic representations of redox exsolution, (b) SOC gas reduction (5% H_2/N_2) (c) electrochemical switching (by applying 2 V across the cell) and a typical exolved Ni on titanate electrode structure [47], see also section 14. Reprinted by permission from Springer Nature Customer Service Centre GmbH: Nature, Nature [47] © 2016.

electrode with oxide electrolyte is another challenge, required to reduce the sintering temperature of electrolyte materials. Symmetrical reversible SOFCs based redox perovskite oxides as the electrodes will be a promising electrochemical device for both energy conversion and storage.

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6. Perovskite solid oxide cell electrolytes

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6.1. Status

Exploring the widespread use of oxide ion conductors for solid-oxide fuel cells, ion pumps, and various sensors leads us to anticipate advanced and efficient energy conversion and storage technologies in the near future. Oxide ion conductors mainly consist of two categories: fluorite-based oxides (AO_2) and perovskite oxides (ABO_3). Over the past few decades, yttria-stabilized zirconia (YSZ), a fluorite-based oxide ion conductor, has been extensively used as an electrolyte in solid electrochemical devices. However, its high operation temperature and lower conductivity in the lower temperature ranges for such devices were major drawbacks [51, 52]. Nowadays, alternative oxide conductors with lower operating temperatures are under continuous investigation such as doped ceria and lanthanum gallate perovskite oxides, which critically rely on novel, higher-performance, and lower-cost dopant materials. These efforts have confirmed superior solid-state electrolytes for chemical-to-power and power-to-chemical applications such as solid oxide fuel cells (SOFCs), solid oxide membrane electrolysis, hydrogen generation, syngas production, and CO_2 reduction [46, 53, 55–57].

Perovskite oxides are described by the general formula ABO_3, where the A cation is conventionally larger than the B cation and the total cation charge of A and B is 6+, where A is a divalent (2+) or trivalent (3+) cation and B is a tetravalent (4+) or trivalent (3+) cation. The typical lattice structures are corner-sharing BO_6 octahedral with small-sized cationic 6-fold coordination, in which the A site occupies the resulting cub-octahedral cavities in the 12-fold coordination arrangement. In the perovskite lattice, both the A and B sites can be partially substituted with cations of lower valence, which can easily form large amounts of extrinsic vacancies in the oxygen sub-lattice to maintain electro-neutrality and thereby promote the migration of oxygen ions through the lattice [57, 58]. For example, Ishihara *et al* reported in 1994 that the Sr^{2+}- and Mg^{2+}-doped $LaGaO_3$ (LSGM: $La(Sr)Ga(Mg)O_{3-\delta}$) perovskites showed fast ionic conduction in the extrinsic vacancies [53]. Subsequently, several groups have optimized and investigated this novel perovskite electrolyte for use in intermediate-temperature SOFCs [59], since the oxide ion conductivity of synthesized LSGM is three times higher than that of YSZ [53]. Perovskite oxide electrolyte strategies are illustrated in figure 12.

Following the pioneering work on LSGM as a superior ionic conductor, several groups have contributed significantly to developing and applying not only perovskite electrolyte but also novel perovskite electrodes for state-of-the-art next-generation SOFCs [46, 54, 59]. However, a few essential requirements must still be addressed for the widespread use of commercial perovskite-based electrolytes in electrochemical applications, such as designing cost-effective compositions and improving the mechanical properties, ionic conductivity, and chemical compatibility between electrolyte and electrode materials. Nevertheless, the $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$, in which the stoichiometry of the A/B sites is adjusted by Sr and Mg, is still the most interesting perovskite electrolyte system.

6.2. Current and future challenges

In the decades since LSGM was successfully validated for intermediate-temperature SOFCs, perovskite oxide electrolytes have rapidly emerged. However, their lower mechanical strengths and higher reactivity with electrodes compared to the YSZ electrolyte makes it difficult to find compatible materials and remain major challenges. To improve perovskite electrolytes, several goals have been recognized: (a) stable chemical compatibility, (b) improved ionic conductivity, (c) suitable mechanical properties, and (d) cost-effective compositions. In this regard, effective strategies including the design of compositions completely distinct from traditional perovskite cubic structures, tuning of existing compositions, and finding new approaches to manufacturing and device configuration must be established.

In terms of the phase stability and mechanical strength of $LaGaO_3$-based structures, stoichiometry issues at the Ga site with partial substitution must be considered. To date, few efforts have addressed the high difficulty of obtaining pure-phase $LaGaO_3$ perovskites because of the slightly volatile Ga site balance during high-temperature manufacturing, although it has a negligible impact on the overall electrochemical performance. The design of stoichiometric or non-stoichiometric A/B sites in $LaGaO_3$ could improve the conductivity and chemical stability of the LSGM electrolyte because such changes tend to maintain the perovskite structure while affecting the defect balance and structural parameters of the host lattice [59]. A recent report showed that composition control by tuning the non-stoichiometry of the A and B sites or Ga excess in the LSGM structure leads to more oxygen vacancies in the perovskite lattice and thus an improved

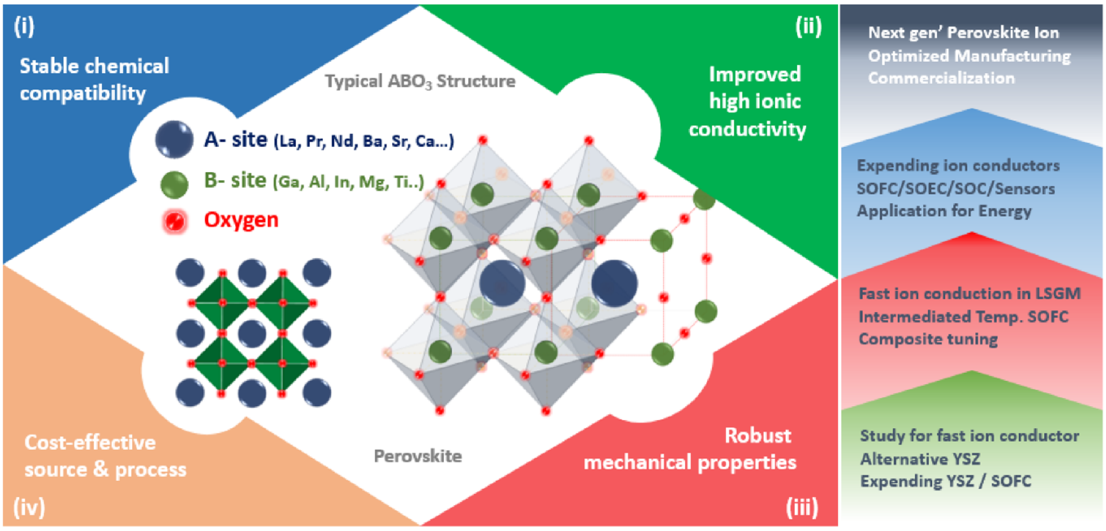

Figure 12. Perovskite ion conductor ABO_3 typical structure and the requirements faced in the roadmap.

oxide ionic conductivity [60]. Furthermore, the loss of oxygen and subsequent formation of oxygen vacancies, which are related to changes in the lattice volume, might involve a structural phase transition between cubic ($La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_3$ [61]), orthorhombic, and rhombohedral at high temperatures. However, for the same vacancy concentration between non-stoichiometric A and B sites, it has been reported that B-site defects improve the thermal stability by maintaining the lattice structure and suppressing the diffusion rate of A-site cations [65]. In any case, it is clear that improved properties can be obtained by non-stoichiometric A/B sites in the perovskite oxide electrolyte. However, it is still essential to further understand the defect chemistry, charge carrier mechanism, and phase stability in the LSGM lattice.

From the perspective of manufacturing, the major difficulty with the $LaGaO_3$-based electrolyte is its incompatibility with commercial electrode materials during high-temperature processes. Especially, Ni-based materials result in the formation of an insulating impurity phase at the interface between the electrolyte and electrode, which blocks ionic pathway. Thus, several interlayers to prevent the reaction between LSGM and other electrodes have been introduced for LSGM commercialisation [59]. A-site cation diffusion into electrode materials is associated with Ga excess phases such as $LaSrGa_3O_7$, which is an insulating impurity at the interface in these electrolytes [62]. This has hindered developments towards a high performance even by reducing the thickness of the perovskite electrolyte, using state-of-the-art electrode materials, and adopting new manufacturing processes. Recently, the feasibility of a thin LSGM on a ceramic anode support, which exhibits no serious interfacial reactions because of the non-stoichiometric Sr/Mg balance and Ga-excess B sites, was demonstrated for $(La_{0.9}Sr_{0.1})_{0.98}(Ga_{0.8}Mg_{0.2})O_{3-\delta}$ with a maximum power density of 1.12 W cm^{-2} in a thin-film perovskite SOFC [63]. However, the performance degradation from interfacial reactions with Ni-based and other electrodes remains a major drawback for perovskite oxide electrolyte applications in the near future. Therefore, by establishing strategic stoichiometric/non-stoichiometric approaches, not only to improve the electrolyte thermal/mechanical stability but also to avoid Ni diffusion and insulating impurities by better understanding the thermodynamics and crystal structure details would greatly aid in the development of efficient next-generation energy conversion and storage devices. Furthermore, technical engineering approaches to realize a practical superior electrochemical performance with perovskite electrolytes as a new pathway for innovative manufacturing (low-priced additives, thin films, high-speed sintering, *in-situ* exsolution on the electrolyte surface, low-temperature sintering, etc) and novel cell configurations are also strategies for solving the discussed issues.

6.3. Advances in science and technology to meet challenges

Improving the ionic conductivity, mechanical properties, and chemical compatibility of perovskite oxide electrolytes would allow their use to be extended to a wider range of applications including SOFCs, solid oxide electrolysis cells (SOEC), hydrogen production, syngas reactors, membrane reactors, and CO_2 conversion. Despite the continuous exploration of brand-new perovskite oxide compositions, no promising alternative to LSGM as an intermediate-temperature electrolyte has yet been found. For instance, a new disordered hexagonal perovskite conductor exhibiting both ion and proton conductivity was recently reported by Fop *et al* [64]. Lately, protonic perovskite oxide electrolytes have gained interest as next-generation materials, and related protonic oxide electrolytes will be covered in detail in section 7. Recent A/B-site non-stoichiometric tuning and understanding of the lattice structure have led to improvements to the chemical/thermal compatibility, conductivity, and thermodynamic understanding [60, 65]. Especially, Ga-rich impurities including $LaGaO_4$ and $LaGa_3O_7$ were identified in detail through studies on the thermodynamics of ternary systems [58], interstitial oxides with melilite structures [66] and the thermo-mechanical properties of A/B-site-deficient compositions [65]. However, a full understanding of the defect chemistry mechanism in the lattice and the mechanical properties remains necessary to improve the commercial aspects.

Scientific efforts to solve the above issues continue, but the manufacturing and engineering design of new perovskite oxide electrolytes must also be approached for practicality. In particular, LSGM has mostly been demonstrated in intermediate-temperature SOFC applications. Going forward, it is necessary to improve the commercialisation of electrolyte materials, and if the above-mentioned strategies are achieved, the value of perovskite electrolytes will be extended to solid oxide electrolysis, CO_2 reduction, and the syngas sector. For this progress, in addition to upgrading current processes, state-of-the-art approaches such as *in-situ* exsolution of functional electrodes (see section 13) must also be attempted through newly designed devices or novel manufacturing processes. Barnett *et al* suggested a good example of potential reversible solid oxide cells as large-scale energy storage and conversion devices using the LSGM electrolyte [67, 68]. However, in terms of marketing and considering the manufacturing and engineering level of LSGM, large-scale powder synthesis processing, efficient sintering, and other procedures must be addressed together. Advanced strategies, such as scientific approaches, simulated composition designs, and manufacturing innovations with AI techniques, could solve the various discussed problems. For this, a fundamental understanding of the thermodynamics, crystalline material chemistry, and physical properties must first be achieved.

6.4. Concluding remarks

As these technologies come to commercial reality, the durability and reliability of solid electrochemical devices operated at high temperatures become more important. Consequently, efforts to reduce the operating temperature have been made through alternative fast ionic conductors, which benefit the life cycle of all surrounding components by lowering the temperature. Particularly, the discovery of LSGM as a perovskite oxide electrolyte has provided a stepping stone for next-generation SOFCs/SOECs. Perovskite oxides have significant promise as alternatives to oxide ion conductors, and as-discussed above future approaches are expected to contribute greatly to developing better perovskite systems. It remains a major challenge to concurrently understand the defect chemistry in the tuned lattice and design the electrochemical and physicochemical properties, especially regarding incompatibility with NiO and cost-effective manufacturing designs for the commercial industry. Superior electrochemical performance has to be achieved with the commercial devices, which have succeeded in developing thin perovskite electrolyte by applying an inexpensive large-area coating process enable of suppressing reaction with other electrodes through outstanding robust tuned composition from the previous one including LSGM and should be studied.

Acknowledgments

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7. Protonic solid oxide cell electrolytes

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7.1. Status

Proton-conducting oxides are considered to be potential next-generation materials for energy conversion and storage with the advantage of high proton conductivity at intermediate temperatures of 350 °C–650 °C [69, 70]. Unlike oxygen ion conducting oxides and proton-conducting polymers, proton-conducting oxides (so-called protonic ceramics) possess the distinctive feature that protons can rotate and transfer around the lattice oxygen ion, in lieu of accommodation in the lattice, with low activation barriers under reducing or humid conditions. This transport peculiarity potentially enables proton-conducting oxides to serve as solid-state electrolytes for chemicals-to-electricity and electricity-to-chemicals (including hydrogen evolution and purification, syngas production, ammonia synthesis, and methane dehydroaromatization) applications [72–75].

Since Iwahara's discovery of proton conduction in perovskite oxides in 1980 [75], state-of-the-art protonic oxide electrolytes tend to converge towards cerate and zirconate based simple perovskite oxides ($A^{2+}B^{4+}O_3$), as historically illustrated in figure 13. The essential requirements have been established to engineer protonic oxide electrolyte: low distortion from cubic structure and large unit cell allowing more oxygen vacancies to favour proton formation and mobility upon hydration; high basicity of B-site cations (or low electronegativity) facilitating proton incorporation; chemical compatibility with anode and cathode compositions, and chemical resistance to acidic atmospheres (such as H_2S, H_2O and CO_2). Following these principles, the strategy of non-stoichiometry created by 20 atom % Y incorporation into the B site within the solubility limit show the most promising acceptor doping among Sc, Ho, Pr, Sm, Nd and other rare earth candidates, offering extrinsic oxygen vacancies and thus improving proton conductivity. The further partial substitution of Yb for Y could enhance proton conductivity and chemical stability against H_2O and CO_2 atmospheres. Despite advances in proton-conducting electrolyte design, manufacturing and processing need to be improved to achieve a dense electrolyte. Due to the poor sinterability of $BaCeO_3$–$BaZrO_3$ based ceramics, a small amount of sintering aid (such as ZnO, CuO, CoO and NiO) is added to densify the electrolyte, as well as lowering the sintering temperature on the premise that the sintering aids have little detrimental effect on proton conductivity.

Apart from $BaCeO_3$-$BaZrO_3$ simple perovskites, complex perovskites like double perovskites and derivatives, including $Ba_2In_2O_5$, $Sr_2Sc_{1+x}Nb_{1-x}O_{6-\delta}$, $Ba_3Ca_{1+x}Nb_{2-x}O_{9-\delta}$, and $Ba_3Ca_{1+x}Ta_{2-x}O_{9-\delta}$, are proton-conducting alternatives in current and near-term researches [76]. Unfortunately, doped $Ba_2In_2O_5$ materials suffer decomposition under reducing atmospheres, especially at elevated temperatures, which impedes the electrochemical application for electrolytes. Among them, the best-known members of perovskite derivatives, $Ba_3Ca_{1.18}Nb_{1.82}O_{9-\delta}$ (BCN18) and $Ba_3Ca_{1.18}Ta_{1.82}O_{9-\delta}$ (BCT18), exhibit conductivities comparable to $BaCeO_3$-$BaZrO_3$ systems, but also are resistant to CO_2 and humid atmospheres, indicating a potential proton-conducting electrolyte. Very recently, the newly developed hexagonal perovskite $Ba_7Nb_4MoO_{20}$ shows high oxygen ion and proton conductivity (the bulk conductivity is 4.0 mS cm^{-1} at 510 °C), as well as excellent chemical and electric stability [64]. Note that an acceptable ionic conductivity of electrolyte for a ceramic fuel cell should be more than 0.01 S cm^{-1}. Obviously, most proton-conducting perovskite families perform superior conductivity than oxide ion conductors in the intermediate temperature range, especially for highly textured BZY films that can be achieved by PLD processing [77], as shown in figure 14.

7.2. Current and future challenges

The major issue encountered in protonic electrolytes is ascribed to low grain boundary conductivity, which is lower by two orders of magnitude than bulk conductivity. This behaviour is primarily due to the refractory nature of Zr, leading to small grain size and poor sinterability. Despite the increase of Ce content increasing conductivity and sintering improvement, the presence of Zr allows a tradeoff between performance and chemical stability. Efforts to further reduce grain boundary resistance have focused on introducing sintering aids to decrease the grain boundary density and enhance grain growth, associated with lowering sintering complexity. Nonetheless, full understanding of these sintering aids still needs to be achieved due to the fact that these can accumulate in grain boundary regions. Note that no best effective strategy has yet been imposed to thoroughly eliminate the grain boundary barriers.

The desirable proton-conducting electrolyte should remain stable under various conditions for practical applications, involving in chemical stability when exposed to high concentration of CO_2 and H_2O, chemical compatibility with anode and cathode components, negligible degradation during long-term fuel cell and

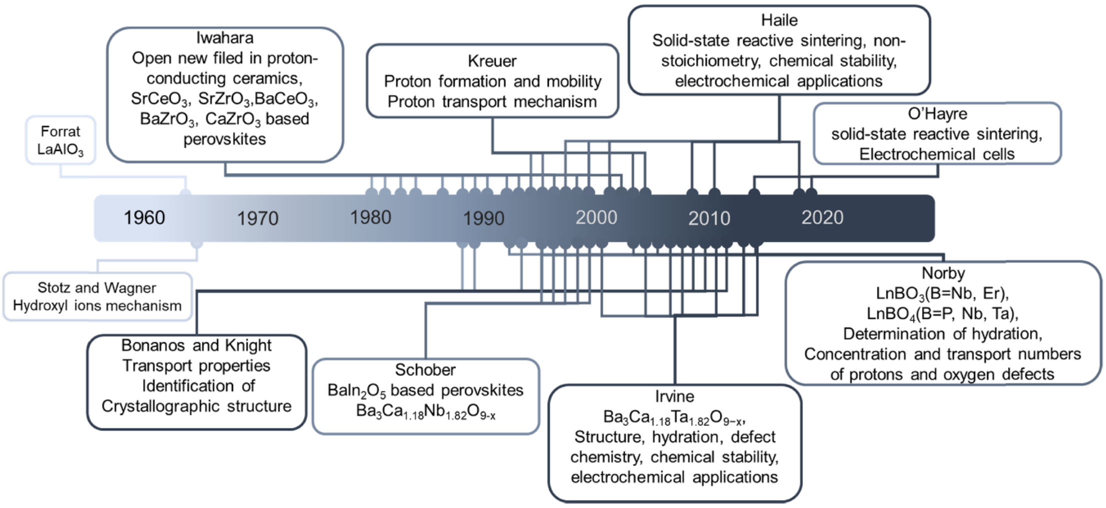

Figure 13. The timeline of main discoveries in proton-conducting perovskite oxides.

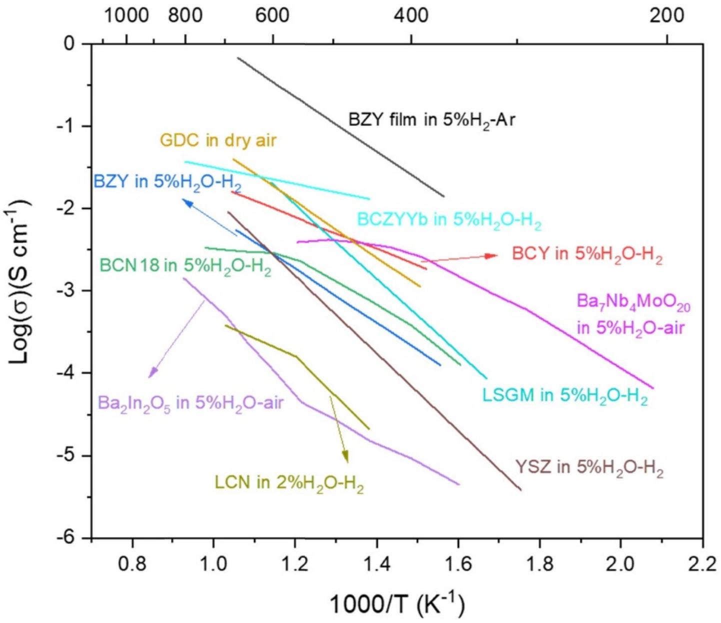

Figure 14. Arrhenius plots of total conductivities of state-of-the-art oxygen oxide and proton conductors [78]. Reprinted from [78], Copyright (2021), with permission from Elsevier.

electrolysis cell operation. The truth is that impurity phases emerge after stringent treatment of CO_2 and H_2O, and ions readily diffuse between air electrode and electrolyte under harsh environments, even though $BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3-\delta}$ electrolyte seems stable with extremely low fuel stream during >8000 h operation [79]. In addition, the hydration and dehydration reactions occur over an operating temperature range rendering the changing thermal expansion coefficients. It is difficult to seek a suitable air electrode to match with the electrolyte.

As mentioned above, oxygen vacancies in oxides are necessities for proton transport, implying proton conduction is associated with oxide ions and electron holes relying on operating conditions. For example, pure proton conduction only exists under wet reducing environments and low temperatures. That means handling in dry and oxidizing conditions could suppress proton transport, leading to high activation energy and cause electron leakage. Though some thermodynamic calculations determine three charge carriers, it is a great challenge to quantify them in terms of current characterization technologies. We aim to build strategies to maximize proton conduction and avoid electron leakage by understanding the correlation of defect chemistry and transport properties, tailoring the compositions of the electrolyte, optimizing manufacturing parameters and adjusting operating conditions.

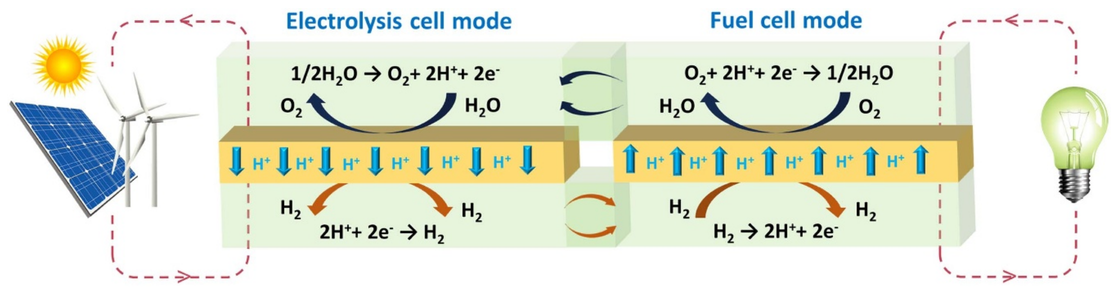

Figure 15. A schematic of sustainable protonic electrochemical cells.

7.3. Advances in science and technology to meet challenges

Current efforts have yet to establish approaches to deliver significant roll-out. Despite various well-established synthesis technologies, the pursuit of suitable sintering aids and the strategies of non-stoichiometry have been developed to improve proton conductivity, promote grain growth and thereby reduce high resistive grain boundaries. For instance, recently reported $BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3-\delta}$ electrolyte fabricated by NiO-assisted solid-state reaction has demonstrated excellent performance and durable stability in both fuel cell and electrolysis cell mode [80]. Meanwhile, a modified $BaCe_{0.4}Zr_{0.4}Y_{0.1}Yb_{0.1}O_{3-\delta}$ composition but with dense cathode interlayer by pulsed laser deposition shows an exceptional peak power density of 1.3 W cm^{-2} at 600 °C in lab scale-up dimension [81]. Interestingly, the electrolyte produced by solid-state reaction tends to be rather more stable than that in wet chemical synthesis, largely due to larger grain size and low grain boundary density achieved in solid-state reaction. In this regard, these advances provide deep understanding of manufacturing and processing to drive protonic electrolyte step forward.

A- and B-site non-stoichiometry on parent perovskites can control the correlation of structural, stability, transport and catalytic properties. Doping strategies with Pr, In, Gd and Nd into B site have been reported to improve the conductivity and stability moderately [82]. Especially, simultaneous substitution of 10 mol% Y and 10 mol% Yb for Ce and Zr show the optimal result, though a full understanding of defect chemistry mechanism is not well completed. Likewise, NiO-assisted solid-state reaction leads to the formation of Ni-doped BCZY composition, readily enabling *in situ* exsolution of Ni nanoparticles anchored on the BCZY surface under reducing conditions that is responsible for the enhancement of performance and durability [79]. Creatively, an electron doping strategy is able to introduce protons into $SmNiO_3$ perovskite via hydrogenation without oxygen vacancies and demonstrate a promising electrolyte for proton ceramic fuel cells [83]. This strategy may break the bondage of conventional Grotthuss mechanism, providing a new pathway to guide further exploration.

Given the fact that the strategy of non-stoichiometry creates more oxygen vacancies to enable proton incorporation and transport but impart unnecessary mixed oxygen ion and hole conduction, it is not easy to accurately distinguish three charge carriers in proton-conducting oxides. Fortunately, both experimental and calculational findings [84, 85] verify the strong influences of temperature, vapour partial pressure (PH_2O), and oxygen partial pressure (P_{O_2}) on transport properties. Thus, the fundamental understanding of the relationship between thermodynamic quantities and defect equilibrium modelling can establish concise principles to map the concentration, transference number and conductivity measurement of each charge carrier.

7.4. Concluding remarks

Oxides with perovskite-type structures show great potential as protonic electrolytes. Recent advances have been focused on simple $A^{2+}B^{4+}O_3$ perovskites ($BaCeO_3$-$BaZrO_3$ systems), and other new perovskite derivatives should continue to be sought. By control of non-stoichiometry and screening techniques, innovative solid-sate perovskite materials with suitable proton conductivity at much lower temperatures (<400 °C) are urged to be sought. With advances in material science and deep understanding of composition-structure-property relationships, some critical technologic issues should be overcome to meet practical requirements. Current research evidences suggest that proton-conducting perovskites are the most envisioned materials for the near-future SOFC commercialization (figure 15). To this end, optimization of manufacturing, sealing, thermal cycling, system design, fuel choice and balance-of-plant are key concerns.

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8. Protonic solid oxide electrodes

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8.1. Status

As described in the preceding section, the relatively recent (∼1980) discovery of oxides that permit solid-state proton conduction has led to the exciting emergence of several potentially transformative electrochemical technologies, including protonic-ceramic fuel cells (PCFCs) and electrolysis cells (PCECs), electrochemical sensors, and proton-based membrane reactors [70]. The unique intermediate temperature regime (∼350 °C–650 °C) of protonic oxides (as compared to low-temperature liquid or polymeric ion conductors and high-temperature solid oxide oxygen-ion conductors) confers important advantages: high efficiency, stability, electrochemical versatility, and low materials cost. However, in nearly all applications, device performance and functionality are currently limited by the lack of electrode materials expressly designed for protonic oxide integration.

State-of-the-art electrode materials for these devices are predominantly perovskite oxides (ABO_3), which are well-suited to the requirements of electrodes: they readily accommodate high concentrations of ionic and electronic defects, and their properties can be tuned via both cation and anion substitution. Negative electrodes must be electrochemically stable under highly reducing conditions and at low potentials (typically −0.2 to 0.2 V vs. standard hydrogen electrode (SHE)), while positive electrodes require stability under highly oxidizing conditions and at elevated potentials (typically 0.5–1.5 V vs. SHE). Ceramic-metal composites, typically comprising of Ni and a proton-conducting perovskite such as $BaZr_{1-x}Y_xO_{3-\delta}$ (BZY) or $Ba(Ce,Zr,Y,Yb)O_{3-\delta}$ (BCZYYb), serve as fuel-flexible, coke- and sulphur-resistant negative electrodes [86]. State-of-the-art positive electrodes often exhibit mixed electron, proton, and oxide-ion conduction. These materials, known as triple ionic-electronic conductors (TIECs), enable high oxygen reduction and oxygen evolution reaction (ORR/OER) activity [70, 87].

Despite rapid progress in PCFCs and PCECs, further advances in electrode materials, especially for the positive electrode, are necessary to fully realize the benefits of their unique operating temperature range. Improving the positive electrode's low-temperature performance and stability under varying conditions could enable commercially viable protonic ceramic devices for efficient power generation and renewable hydrogen production. In addition, though most work to date has focused on fuel cells and electrolyzers, next-generation protonic ceramic electrochemical devices present diverse opportunities for chemical production, fuel upgrading, and energy storage, as highlighted in figure 16 [70]. Protonic ceramic electrode materials have even shown promise in other energy applications, such as alkaline fuel cells and Li-air batteries, presenting opportunities for cross-cutting learning and development.

8.2. Current and future challenges

In PCFCs/PCECs, the overpotential at the positive electrode tends to dominate polarization losses, especially at relatively low temperatures, due to the high activation energy of the ORR/OER [70, 74, 88]. The ORR/OER and water evolution/uptake depend on the rates of surface oxygen exchange and defect transport. In the absence of ionic conductivity in the positive electrode, these reactions are constrained to triple phase boundaries (TPBs) between the electrode, electrolyte, and gas phases. In principle, TIEC positive electrodes expand the electrochemically active area to the entire gas-electrode surface, as illustrated in figure 17. Although this incentive has stimulated extensive study of TIEC positive electrodes, the positive electrode remains the limiting component of intermediate-temperature ceramic cell performance.

The lifetime of protonic ceramic cells is limited by the stability of the electrodes. The high steam concentrations present at the positive electrode under realistic operating conditions are particularly challenging to chemical stability. State-of-the-art electrode materials usually employ Ba and/or Sr at the A-site, taking advantage of their basicity, which promotes proton uptake but also decreases chemical stability [89]. Meanwhile, Co is often substituted for the B-site in positive electrodes to impart ORR activity and electronic conductivity due to its facile transition between 3+ and 4+ oxidation states. Unfortunately, this same redox behaviour yields poor chemical stability coupled with thermal expansion coefficients exceeding those of standard electrolyte materials [88], threatening mechanical stability. These stability-performance tradeoffs limit the potential of existing materials.

Design of improved electrode materials is hindered by a lack of understanding of the physicochemical mechanisms in protonic ceramic electrodes. This is largely because it is challenging to deconvolute transport of three distinct charge carriers, especially when considerable electronic conductivity masks ionic contributions [87]. Additionally, coupling between surface reactions and transport pathways makes it

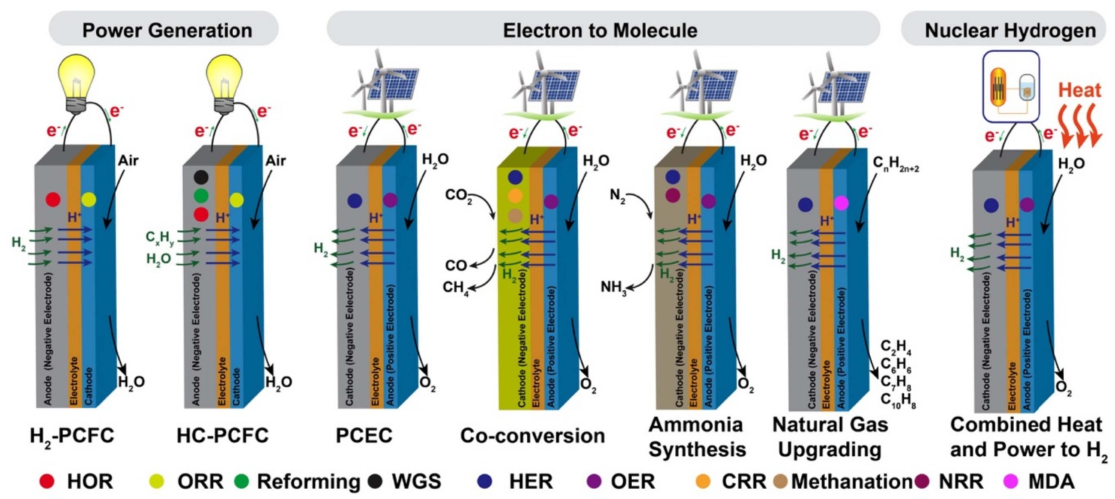

Figure 16. Current and envisioned applications of protonic ceramic devices. PCFC = protonic ceramic fuel cell; PCEC = protonic ceramic electrolysis cell; HC-PCFC = hydrocarbon PCFC; HOR = hydrogen oxidation reaction; ORR = oxygen reduction reaction; WGS = water-gas shift; HER = hydrogen evolution reaction; CRR = carbon dioxide reduction reaction; NRR = nitrogen reduction reaction; MDA = methane dehydroaromatization. Reprinted from [70], with the permission of AIP Publishing.

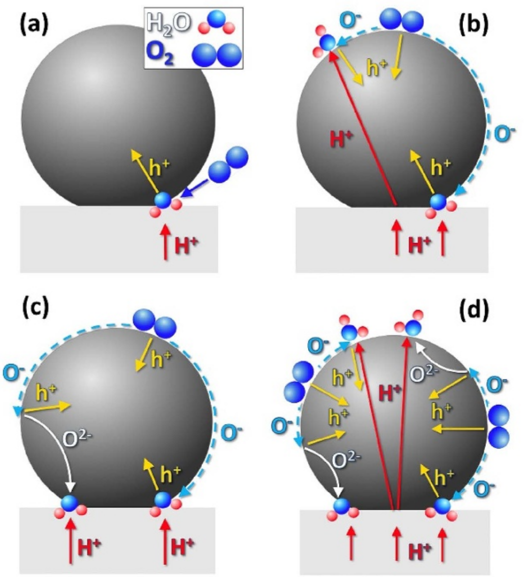

Figure 17. Possible transport and reaction pathways in a positive electrode particle contacting the electrolyte in a PCFC. Each panel considers different mobile charge carriers in the positive electrode. Electronic charge carriers are represented as holes. (a) Electronic conduction only: the ORR and water formation can proceed only at the triple phase boundary between electrolyte, electrode, and gas phases. (b) Mixed proton and electronic conduction: protons can travel to the electrode surface to react with adsorbed oxygen and form water. (c) Mixed oxide ion and electronic conduction (MIEC): oxygen can be reduced at the electrode surface, but must travel to the triple phase boundary to react with protons and form water. (d) Mixed proton, oxide ion, and electronic conduction (TIEC): oxygen can be fully reduced and react with protons at any point on the electrode surface. Reprinted by permission from Springer Nature Customer Service Centre GmbH: Nature, Nature Materials [87] © 2020.

difficult to isolate and probe these processes experimentally [90]. One outstanding enigma is the role of proton conduction in the positive electrode: mixed oxide ion and electron conducting positive electrodes perform effectively in PCFCs despite their lack of proton conductivity [70], suggesting that our understanding of the active mechanisms is incomplete. This lack of fundamental knowledge makes it difficult to effectively develop new electrode materials or tune existing materials.

8.3. Advances in science and technology to meet challenges

Researchers are pursuing a variety of innovative electrode design strategies to address stability and performance challenges. Positive electrode-electrolyte interlayers formed by pulsed laser deposition can enhance charge transfer between the electrolyte and positive electrode and provide a thermal expansion buffer [74]. Carefully engineered composite electrodes can maximize TPB area and allow tailoring of bulk and surface properties [70]. Additionally, layered perovskite electrodes may enhance oxygen transport via high-diffusivity pore channels [91], although there remains some doubt regarding whether or not these materials retain their layered structures under operating conditions. There are also some efforts to develop Ni-free, fully ceramic negative electrodes, which are discussed in greater detail in section 5.

Neither a comprehensive understanding of electrocatalysis in protonic oxide electrodes nor an efficient technique to probe the contributions of different charge carriers and reaction pathways has yet been developed. Beamline techniques, isotope tracer studies, and *in-situ* spectroscopy can be of great utility here, but they are time-consuming and expensive. Electrochemical impedance spectroscopy (EIS) has long been the standard in electrochemical characterization of electrodes, but the interpretation of results using equivalent circuit models is often ambiguous. EIS analysis via the distribution of relaxation times provides greater resolution of convoluted physical processes and may contribute to improved physical models [92]. Non-linear EIS, which has recently been applied to solid oxide fuel cells and Li-ion batteries, provides complementary information to conventional EIS that may help more definitively identify the appropriate physical model, though it requires complex analysis [90]. These emerging analytical techniques present a pathway to greater understanding of electrode processes without requiring exhaustive, multi-tool characterization.

Despite intensive investigation of TIEC electrodes, the lack of clear design principles for these materials has largely constrained TIEC development to empirical modifications of known mixed or triple ionic-electronic conductors. However, some current efforts take a more extensive and systematic approach, harnessing high-throughput computation and experimentation to rapidly screen large numbers of candidate materials [88]. The integration of machine learning models with these techniques may help uncover important composition-structure-property relationships and guide further exploration [93]. This data-driven screening process promises to accelerate the pace of TIEC development.

8.4. Concluding remarks

Perovskite oxides provide a versatile framework for tailoring electrocatalytic activity in protonic ceramic devices, but the expertise to effectively manipulate performance must be further developed. Concerted efforts to engineer electrode microstructures and develop an understanding of degradation and rate-limiting mechanisms are driving steady improvements in performance. Meanwhile, systematic studies of composition-property relationships are beginning to establish design principles that may soon allow leaps in materials discovery. Leveraging these developments to improve the stability and low-temperature activity of electrode materials will be key to realizing the full advantages of protonic ceramics for energy conversion.

Acknowledgments

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9. Bifunctional perovskite electrocatalysts for ORR and OER

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9.1. Status

The efficiency of renewable-energy technologies that rely on the electrochemistry of oxygen, such as rechargeable metal-air batteries and regenerative fuel cells is hindered by the kinetic limitations of the oxygen electrocatalysis, i.e. the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER), occurring at the electrodes of these devices (ORR: cathode of a battery/fuel cell, OER: anode of an electrolyser) [94]. Most studies focus on either the ORR or OER reactions, but for battery applications, such as Zn/air or Li/air, and regenerative fuel cells the ideal electrocatalyst will be suitable for both reactions. Achieving efficient bifunctional catalysis requires minimisation of the overpotentials for both reactions and is commonly determined by measurement of the difference between the potentials required to attain a desired current density for both reactions [95].

Perovskite oxides of the general formula ABO_3, where A is a large-radius rare-earth ion and B is a transition metal ion, have attracted increasing interest and hold great promise as efficient OER electrocatalysts to replace noble-metal-based catalysts especially in alkaline media, owing to their high intrinsic catalytic activity, abundant variety, and low cost, and rich resources [96]. They generally have lower ORR activity, but their capability of accommodating partial substitution at the A and/or B sites ($A_{1-x}\,A'_xB_{1-y}B'_yO_3$), introducing changes in the valence states of the metal cations and oxygen vacancies, provides a compositional landscape that continues to be explored in an effort to find the most active/durable/economic electrocatalysts. Materials are prepared both as thin films deposited on to a substrate and as (nano)particulate materials. The latter have been prepared using a range of methods including solid-state synthesis, combustion, precipitation, hydro/solvothermal synthesis, sol-gel synthesis, and polymer-assisted approaches [95]. As the compositional landscape continues to be explored, greater understanding of the fundamental structure-property relationships for these materials increases. Exploration of preparation methods will deepen understanding of the role of particle size and texture in determining activity and durability of the materials. In addition the preparation of composite materials, incorporating conductivity enhancers and co-catalysts may enable some of the inherent limitations of the materials to be overcome.

9.2. Current and future challenges

The fundamental understanding of bifunctional ORR/OER electrocatalysis at perovskite electrodes has developed rapidly in the last decade. Such work has been dominated by exploration of the compositional landscape, with the aim of either finding the most active materials by screening a large number of materials or to establish activity descriptors, such as e_g orbital filling, metal-oxygen covalency, number of d electrons, position of the d-band centre, the p-band centre of bulk O, equilibrium potential of the B-site cation redox, etc to facilitate such exploration [97]. As mentioned above, most studies focus on either the ORR or OER, and thus neglect to consider the additional challenges posed to achieve efficient bifunctional electrocatalysis. In addressing this particular challenge further work should address the following aspects as depicted in figure 18:

- Mechanistic understanding: The study of most perovskite based electrocatalysts is carried out on (nano)particulate materials and the electrodes themselves contain binders and conductivity enhancers (see below). To fully understand the mechanisms of both reactions, including the effects of the state of the electrocatalyst surface (orientation, defects, surface enrichment, etc) further studies on well-characterized carbon-free preferentially oriented films are required, supported by the development of theoretical models [98]
- Roles of oxygen vacancies: Whilst it is well established that the B-site cations are the redox active sites for ORR and OER the role of lattice oxygen in the mechanisms is less well established [99] and warrants further investigation for both reactions, both experimentally and computationally. Effective strategies to introduce and manage oxygen vacancies include thermal reduction, the introduction of an A-site cation deficiency or substitution of A-site cations with a cation with a lower oxidation state [100].
- Anionic defect engineering: In addition to considering the lattice oxygen atoms as active participants in the ORR and OER mechanisms anion dopants (S/N/P/F) can be introduced to enhance activity by modifying the bulk electronic structure, transport properties, surface adsorption and the formation of sub-surface active

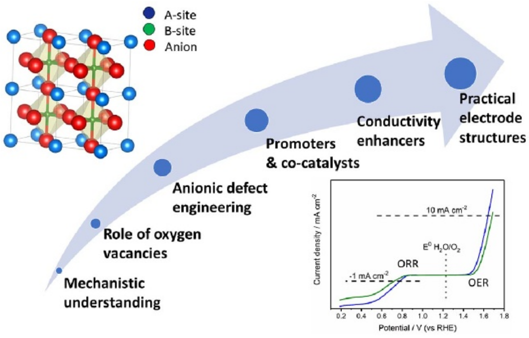

Figure 18. Illustration of the perovskite structure and the compositional/structural landscape that may be explored in seeking the most active/durable/economic bifunctional ORR/OER electrocatalysts.

phases. Greater fundamental understanding is required as greater control of the generation and stability of desired anionic defects [100].

- Promoters and co-catalysts: The gains in activity, measured as the reduction in the overpotential required to achieve a desired current density, achieved for either the ORR or OER reaction, is often off-set by an increase in the overpotential for the other reaction. Adopting the approach of using promoters and co-catalysts from thermal catalysis may represent a means of overcoming this apparent limitation in the design of bifunctional electrocatalysts.
- Conductivity enhancers: Due to the low electronic conductivities of perovskite-type oxides, electrodes often also contain carbon materials, accelerating electron transport [98, 101]. By mixing the oxides with carbon materials, the specific surface area also increases. Many forms of carbon, including graphene, doped graphene, and carbon nanotubes have been explored in recent years. However, greater consideration should be given to the tendency of carbon to corrosion in strong alkali conditions at the potentials for OER as well as recognising the contribution of carbon to the ORR, where it may serve as the active electrocatalyst in alkaline media reducing O_2 to H_2O_2.
- Scaling up the preparation of high surface area materials: Most published studies to date have only considered the preparation of small (10 s of g at most) batches of materials. Whilst the use of small reactors enables greater control over the morphology and nanostructure of the resulting catalysts, considerable effort now needs to be invested in scaling up preparation methods if the materials are to cross over to practical applications.
- *Practical electrode structures:* Performance of perovskite oxides as bifunctional oxygen electrocatalyst at practical current densities has been scarcely reported, with most studies being carried out on thin film electrodes or as thin (nano)particulate catalyst inks deposited on to rotating disc electrodes. To truly operate as a bifunctional electrode at high current densities, the electrocatalyst must be placed into gas diffusion electrode structures that allow both a high flux of O_2 to the catalytic sites during ORR and an effective removal of O_2 away from these sites during OER. An important aspect of work in this area is the effective management of the hydrophilicity of the composite electrode structure to prevent flooding during ORR and drying out during OER.

9.3. Advances in science and technology to meet challenges

Much of the fundamental understanding of the properties of perovskite based bifunctional electrocatalysts originates in silico through the application of density functional theory and materials simulations. A greater application of multi-scale methods is required to describe the evolution of oxygen vacancies and any accompanying structural disorder on the electronic and transport properties of the materials.

Advances are required in the preparation of both model materials, to further fundamental understanding of the mechanisms of ORR and OER and the relative contributions of the B-site cations and surface or lattice oxygen atoms, and (nano)particulate materials using preparation methods that can be scaled up to enable practical applications. Simultaneously further development of *in situ* and operando spectroscopic and structural characterisation methods [102, 103]. In particular advances in near ambient pressure XPS and x-ray Raman spectroscopy enable characterisation of the environments of the surface and lattice oxygen atoms, whilst high energy resolution x-ray absorption near edge structure and x-ray emission spectroscopies probe the effects of applied potential on the oxidation states and coordination environments of the A- and B-site cations. In conducting such measurements the effects of limited mass transport, of O_2, water, protons and hydroxide ions, and any additional effects of increased electronic resistance brought about by the compromises that arise from the modifications to the electrochemical cell design required to enable *in situ* or operando measurements must be taken into account when interpreting the spectra.

9.4. Concluding remarks

The wide compositional landscape offered by transition metal perovskites provides great opportunities in terms of materials discovery for ORR and OER electrocatalysts. Greater consideration needs to be paid to the possible bifunctional nature of such electrocatalysts if they are to find practical application in batteries and reversible fuel cells.

10. Electrocatalysis at perovskite thin films

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10.1. Status

The need to exploit renewable energy sources has resulted in novel approaches to improving renewable energy technologies. Mixed valence metal oxides are of particular interest for a variety electrochemical energy storage and conversion techniques. In particular, inorganic perovskites with the structure ABO_3 (where A and B are metal cations) are experiencing increased research activity as electrocatalysts for the oxygen reactions involved in fuel cells, electrolysers, and metal air batteries [104].

The limiting component of the overall efficiency of a fuel cell is the cathodic oxygen reduction reaction (ORR). The best performing electrocatalysts for this are based on carbon supported Pt nanoparticles. Not only is this material extremely expensive, thus driving the device cost up, Pt is also very prone to catalytic poisoning, which reduces the stability of the catalyst with continuous use. Electrolysers are a related electrochemical technology which can be used to generate H_2 gas by splitting of water. In this process, H_2 is formed via the cathodic hydrogen evolution reaction, but it is the sluggish anodic oxygen evolution reaction (OER) which limits overall device performance. The best OER electrocatalysts are materials such as RuO_2 and IrO_2, whose expense and scarcity render this technology impractically expensive for widespread use. Bifunctional OER/ORR activity is also necessary in unitized fuel cells, which are used for distributed power generation, and in metal-air batteries. OER and ORR have reaction mechanisms specific to acidic or basic media. Metal oxide electrocatalysts exhibit poor stability in acid, necessitating significant improvements in stability, or optimising devices towards alkaline operation.

Mixed valence oxides such as inorganic perovskites are an inexpensive class of materials whose catalytic performance for the OER and ORR can be tailored to rival expensive platinum group metals, at a fraction of the cost. Key to their suitability are the mixed valance cation states and their robust crystalline structure. Rational material design such as substitutional cation doping or formation of anion vacancies can be used to induce cations with specific valence states or electronic structures [105, 106]. This enables the formation of specific surface catalyst sites which are optimized towards a specific reaction (figure 19).

10.2. Current and future challenges

Perovskite synthesis takes place via a number of possible avenues including thermal decomposition, hydrothermal, solid state chemistry, and sol-gel. While these approaches can be readily scaled to produce gram scale quantities of material, the catalyst must be supported on a conductive material to fabricate electrodes for electrocalytic applications. In this context, thin film deposition approaches can be advantageous, as the perovskite layer can be deposited directly on to the conductive support. To this end, a variety of thin film deposition techniques have been investigated; including chemical vapour deposition (CVD) [107], atomic layer deposition (ALD) [108], pulsed laser deposition (PLD) [109], and physical vapour deposition (PVD) [110].

CVD and ALD proceed via the reaction of organo-metallic precursors with oxygen, water, ozone or other oxidising agent at elevated temperatures (approx. 200 °C–600 °C). The synthesis of precursor compounds and differences in their volatility can complicate the overall process. PLD typically uses highly crystalline perovskite targets whose preparation require temperatures in excess of 1000 °C. Evaporative PVD involves thermal heating of source materials in an oxygen-rich environment to grow the perovskite film on a variety of substrates. In all cases above, elevated temperatures are required during deposition in order to form highly crystalline films, additional post-growth annealing is also often employed. These approaches are also best suited to producing only single or a small number of compositions per deposition run. Furthermore, the vast majority of perovskite thin film research to date has focused on photovoltaics, magnetic, superconducting, and dielectric materials, rather than electrocatalysis. Much of the research into thin film deposition of perovskite compounds is focused on hybrid organic-inorganic halide compounds which are widely used in photovoltaic applications, which is outside the scope of this discussion.

10.3. Advances in science and technology to meet challenges

Evaluating the electrocatalytic performance of ternary substituted perovskite thin films requires ease of control over composition. RF plasma techniques have been used to produce atomic oxygen radicals which have a much higher reactivity than molecular O_2. Co-deposition of metals and atomic oxygen in PVD allows the formation of crystalline perovskites on a variety of substrates at relatively low temperatures. This has been demonstrated for a variety of perovskite systems such as Ba $[Sr,Ti]O_3$ [111], Sr $[Ti,Fe]O_3$ [112], and La $[Mn,Ni]O_3$ [113]. Furthermore, the use of compositional gradients and combinatorial approaches has

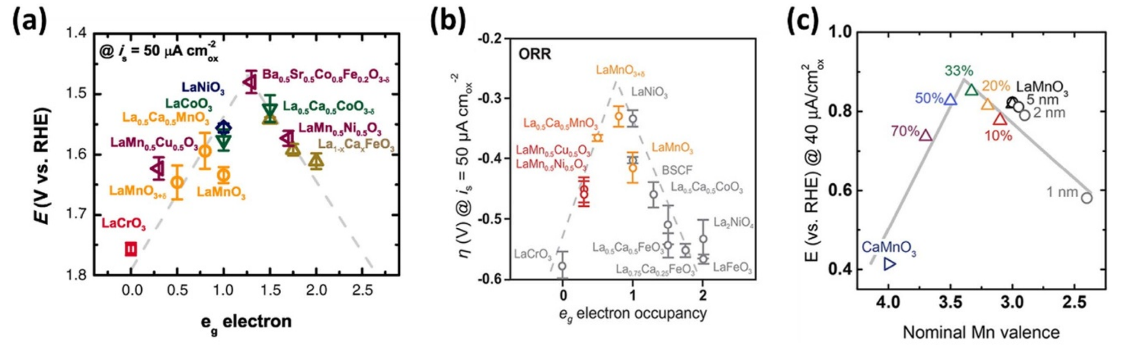

Figure 19. Relationship between (a) OER and (b) ORR overpotential and e_g electron occupancy on B site transition metal for various perovskite catalysts. (c) Influence of Mn valence on ORR activity. (a) From [106]. Reprinted with permission from AAAS, (b) and (c) adapted from [105]. Copyright (2015) American Chemical Society. Activities determined experimentally; electron occupancy and nominal Mn-valence are determined through a combination of experimental and computational techniques.

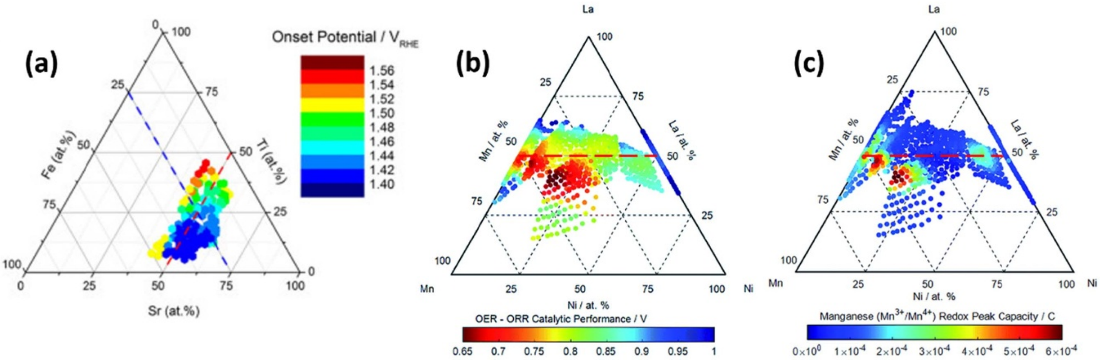

Figure 20. (a) OER onset potential as a function of composition for Sr [Ti,Fe]O_3. Reprinted from [112], Copyright (2018), with permission from Elsevier. (b) Bifunctional OER-ORR activity and (c) charge associated with the $Mn^{3+/4+}$ redox couple as a function of composition for La [Mn,Ni]O_3. Reproduced from [113] with permission of The Royal Society of Chemistry. Red dashed line indicates pseudo-binary perovskite tie-line in each.

facilitated the development of high throughput-PVD, in which large compositional spaces of ternary perovskite systems can be rapidly explored [110]. When deposited on appropriate electrode arrays and coupled with high throughput voltametric measurements, the electrocatalytic performance of large numbers of ternary and quaternary substituted perovskite compounds can be rapidly assessed.

Measurement of activity (in alkaline media) along the pseudo-binary perovskite tie-line from $SrTiO_3$-$SrFeO_3$ revealed that $SrTi_{0.5}Fe_{0.5}O_{3-\delta}$ exhibited the best performance in terms of OER catalysis and electrode stability (figure 20(a)). Higher Fe content resulted in greater OER activity, at the cost of electrode stability, with lattice oxygen participating in the reaction for $SrFeO_3$. These mechanistic insights are important as long-term stability under operational conditions is crucially important for any candidate electrocatalyst. An anti-correlation in OER and ORR activity was observed along the $LaMnO_3$-$LaNiO_3$ pseudo-binary tie-line, with highest OER activity found in Ni-rich compounds of $La_xMn_yNi_{1-y}O_{3-\delta}$.Off this tie-line, it was found that Ni substitutes into both A and B sites for La-deficient compounds. The best performing bifunctional catalyst was found in this region; specifically, $La_{0.85}Mn_{0.7}Ni_{0.45}O_{3-\delta}$. Bifunctional OER/ORR activity was found to correlate with the presence of the $Mn^{3+/4+}$ redox couple (figures 20(b) and (c)). The substitution of Ni^{2+} into the A site of La-deficient compounds creates a mixture of Mn^{3+} and Mn^{4+} through charge balancing, and it is the latter cation which is key to bifunctional activity. This highlights that it is perovskite compounds which lie away from the pseudo-binary tie-line that exhibit the multiple oxidation states which imbue them with great potential in electrocatalysis.

10.4. Concluding remarks

While various thin film deposition approaches have been used to produce inorganic perovskites, there has been relatively little research into electrocatalytic applications of materials produced in this manner, with other synthesis routes favoured. Development of deposition techniques which allow for accurate control over composition and growth at reduced temperatures has enabled the exploration of many ternary substituted doped perovskites as electrocatalysts. This has enabled the untangling of various surface effects and the rational design of novel electrocatalysts tailored to specific reactions. A complimentary approach using computational screening of ternary compounds for desired oxidation states and high throughput experiments will allow for the continued development of the novel inorganic perovskites required to address specific shortcomings in energy conversion and storage technologies.

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11. Heterogeneous catalysis

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11.1. Status

The inorganic perovskite oxides with a general formula of ABO_3 can display a wide range of oxygen nonstoichiometry and offer great flexibility in redox active sites, oxygen vacancies and physico-chemical properties as a result of the numerous possible substitutions with different sizes and valences at both A and B sites. Via tuning the composition and calcination temperature, inorganic perovskites may also be arranged as double perovskite or layered perovskite. With such wide possibilities of compositions and structure, inorganic perovskites have wide applications in many fields as a result of excellent redox behaviour, oxygen mobility, and high electronic/ionic conductivity [114].

Up to now, inorganic perovskites with tunable properties have been extensively investigated in catalysis fields (e.g. photocatalysis, electrocatalysis and traditional heterogeneous catalysis) due to their extraordinary variability of compositions and structures [115]. In the heterogeneous catalysis field, inorganic perovskites with high thermal and hydrothermal stability, tunable acid-base sites and stoichiometries, good redox ability and oxygen mobility have great potential either for gas or solid chemical reactions at high temperatures, or liquid-phase catalytic reactions at low temperatures.

Besides the influence of composition of inorganic perovskites based catalysts on their catalytic performance, their morphology also plays a critical role on catalytic performance in the heterogeneous catalysis field due to its direction to the accessible active sites, such as surface oxygen species, transition metal ions as well as the loaded components on the surface. In the past several decades, various nanostructured inorganic perovskites have been reported and demonstrated to exhibit better performance than their bulk counterparts in catalytic performance, such as for gas oxidation (e.g. CO, CH_4, volatile organic compounds), soot oxidation, reforming reaction for hydrogen and syngas production, selective reduction of NO_x ', whereas their catalytic application in the conversion of biomass to value-added chemicals is still at its early stage (figure 21) [116]. Besides, the improved performance of inorganic perovskites in liquid-phase catalytic reactions has also been reported, such as the selective oxidation of benzyl alcohols, benzylation, esterification, alkylation, hydrogenolysis, aldol addition [117].

11.2. Current and future challenges

The research of inorganic perovskites for heterogeneous catalysis has been developed for several decades, however there are still some challenges to be further addressed.

(a) A key challenge is the difficulty in formation of nanostructured inorganic perovskites due to the usually required high temperature for perovskite-type phase formation and uncontrollable growth paths. Although various methods have been developed to obtain nanostructured perovskites with increased surface areas via the design of particle size and morphology in order to effectively improve their catalytic performance, the preparation of nanostructured perovskites with multi-elements and with desirable morphology, particle size and exposed facets is still challenging, especially for the synthesis of inorganic perovskites with particle size smaller than several nanometers. The accurate synthesis of perovskites with exposed facets and particle size could help precisely understand the influence of perovskite facets and particle size on their catalytic performance.

(b) Another key challenge is to determine the real active species, and the interaction between inorganic perovskites and reactants for specific reactions. Nowadays, the catalytic mechanism or process are usually proposed based on the traditional characterization results (such as x-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), temperature programmed reduction, temperature programmed oxidation) and catalytic performance, but these are generally insufficient to provide hard evidence. The surface composition and active species of inorganic perovskites would also take irreversible change during the catalytic process. To understand the detailed reaction mechanism and the relationship between composition and catalytic activity, more techniques to detect the active species and intermediates for understanding the mechanism are strongly desirable.

(c) To find and design the most effective heterogeneous catalysts via cost-effective strategies is another challenge. Up to now, lots of inorganic perovskites and their supported catalysts have been reported for specific catalytic process, however the comparison and database on the catalytic performance of those inorganic

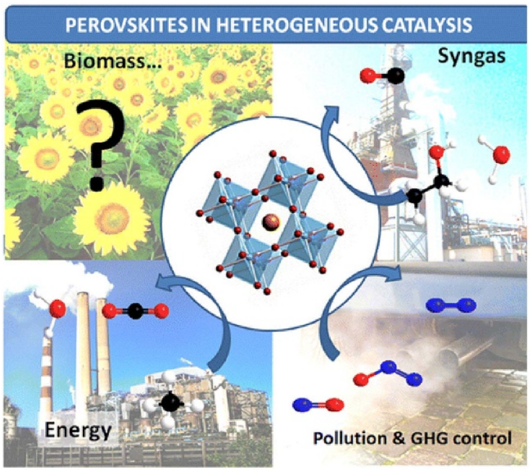

Figure 21. Perovskites in heterogeneous catalysis. Reprinted with permission from [116]. Copyright (2014) American Chemical Society.

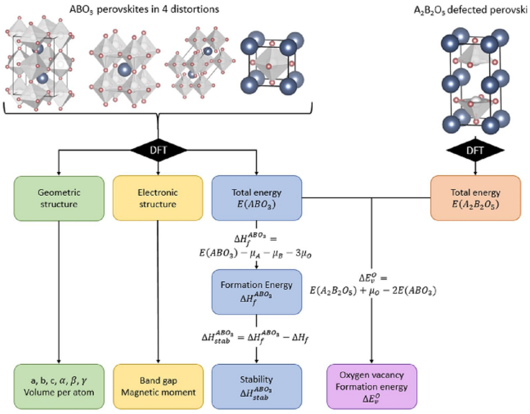

Figure 22. Workflow to calculate all the properties in the current dataset. Reprinted by permission from Springer Nature Customer Service Centre GmbH: Nature, Scientific Data [118] © 2017.

perovskites-based catalysts is still lacking. As a result, scientists and engineers still have to spend a lot of time and cost to try to find the best inorganic perovskite-based catalysts for specific catalytic reactions.

11.3. Advances in science and technology to meet challenges

Up to now, several different methods (e.g. combustion, electrospinning, thermal spray, template and hydrothermal methods) have been reported to prepare nanostructured inorganic perovskites, which display better catalytic performance than their bulk counterparts. Even though these methods all have their advantages and disadvantages, suitable synthesis methods can be adopted to obtain nanostructured inorganic perovskites with increased surface areas and enhanced catalytic performance via optimizing the conditions [119]. In addition, even though it is still challenging, the synthesis of perovskites with tailored crystal facets has also been reported, which could provide some guidance for better design of inorganic perovskite catalysts [120]. To increase the stability of supported metal nanoparticles, exsolved metal or metal oxide nanoparticles can be synthesized via high-temperature reduction and chemical reduction methods [47].

The research and development in advanced *in-situ*/operando characterization techniques, such as *in-situ* TEM, diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS), *in-situ* XPS, *in-situ* x-ray absorption spectroscopy, operando space-resolved and time-resolved DRIFTS-Raman, make it possible to detect the slight but quick changes of surface species and morphology of inorganic perovskite-based heterogeneous catalysts during the catalytic process [121]. Combined with *in-situ* and *ex-situ* characterization, as well as the catalytic performance, the reaction mechanism and the relationship between inorganic perovskites and their catalytic performance can be better understood, which could further promote the development of effective catalysts.

Furthermore in recent years, the development of computer techniques (e.g. machine learning, high throughput screening) and theoretical calculation approaches enable optimisation of composition of inorganic perovskites for specific catalytic process. Building upon this and the known mechanism and knowledge, might greatly reduce the cost and time to find the next generations of catalysts. For example, high-throughput density functional theory calculations have been used for the calculation of formation energies, oxidation states, thermodynamic stability and oxygen vacancy formation energy of ABO_3 perovskites, as shown in figure 22 [118]. In addition, the development of high throughput synthesis and analysis techniques also contribute the further applications of inorganic perovskites in heterogeneous catalysis [122].

11.4. Concluding remarks

In Summary, the surface species and composition in inorganic perovskites mainly determine the intrinsic activity while the apparent catalytic activity could be further improved by constructing nano/micro structures with higher surface areas, more exposed active sites, and enhanced mass/heat transfer ability. With advances in the research and development of synthesis techniques, the synthesis of nanostructured inorganic perovskites with controlled morphology and exposed facets is possible, which could provide deeper understanding about the relationship among composition, morphology and catalytic activity. In addition, modifying the surface with other metal/oxide nanoparticles via deposition or exsolution methods also provides potential strategies for the design of effective inorganic perovskite catalysts with excellent performance. With the development of *in-situ*/operando instrument and computer technique, it is also possible to clearly reveal the changes of the active sites on the perovskite catalysts during the catalytic process and help design more efficient catalysts with low cost, high activity and long durability for special reactions.

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12. Chemical looping

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12.1. Status

Chemical looping (CL) can be defined as a methodology in which an individual reaction can be split into separate subreactions. Each subreaction can be performed in distinct reactors, or in the same reactor at different times. At least one chemical intermediate is transferred, or carried, between the multiple reactors by a carrier material. As such, CL is an 'unmixed' reaction process whereby, e.g. an oxidant and a hydrocarbon can essentially undergo reaction without ever being mixed. Although CL need not be restricted to carrier materials in the solid phase, it is beneficial for products and carriers to be in different phases for ease of separation.

Around 120 years ago a CL process, the steam-iron process (figure 23), was employed for most hydrogen production. Iron oxide is contacted with a reducing gas, usually a reformed hydrocarbon in the form of syngas (carbon monoxide and hydrogen):

$$\text{Iron oxide} + CO + H_2 = \text{iron} + CO_2 + H_2O.$$

Iron is produced along with carbon dioxide and water (with unreacted carbon monoxide and hydrogen). In a second step the iron is reoxidized by steam to produce hydrogen (with unreacted water) that is free of any carbon oxides and thus easily separated:

$$\text{Iron} + H_2O = \text{iron oxide} + H_2.$$

In this example solid iron/iron oxide acts as an oxygen carrier material (OCM) and it remains true that most CL processes studied have relied upon the use of such OCMs.

The recent resurgence of interest in CL is driven by the benefits of inherent product separation such as that of carbon dioxide from flue gas. This topical concern has resulted in the publication of timely texts concerned with energy conversion [123, 124] and beyond [125]. Additionally, progress has been made on improving the stability of OCMs by using more complex, non-stoichiometric oxides, particularly perovskites. Non-stoichiometric perovskites have also been employed in CL processes that, for the first time, have permitted conversions in excess of that allowed by conventional 'mixed' reaction equilibria [126]. Furthermore, CL may allow reactions to be performed under improved operating conditions (see recent work on low pressure ammonia synthesis [127]).

12.2. Current and future challenges

There is no doubt that CL processes could be employed beneficially for a much wider range of reactions. Potential reactions will need to be identified and the contribution of CL evaluated. However, there are as yet no established methodologies for performing such an analysis. Modes in which CL can be utilized have not been fully explored and there is a lack of information on the nature and properties of potential carrier systems. Demonstration of novel modes of operation will require work on e.g. pressure-swing CL (the individual subreactions do not occur at the same pressure), multi-step CL (there are more than two individual steps), the control of fluid-solid contact patterns (fixed beds of carrier can allow equilibrium limitations to be overcome), the use of controlled oxidation and reduction (control of the oxygen chemical potential of a carrier and thus the selectivity of the reactions in which it is involved e.g. partial oxidations). Furthermore, we must deliver carriers of high capacity (i.e. high content of the species to be transferred between subreactions) and high stability. Capacity will need to be readily available (so sufficiently high surface exchange and diffusion coefficients) at the chemical potential required by the process. Modelling will have a role in the prediction of carrier thermodynamic behaviour. Employing composite carriers may allow for systems with more favourable properties but will lead to its own challenges in terms of stability and properties prediction. It may also be necessary to explore the surface modification of carriers in order to enhance surface exchange kinetics.

Finally there will need to be testing under realistic conditions to evaluate the structural and chemical evolution of carriers. Methods for eliminating modes of degradation or reducing their effect will be developed. Reactor and process models will be required to allow testing at scale and prediction of the economic benefits of commercial operation.

12.3. Advances in science and technology to meet challenges

Scientific advances will be required in the areas of *in-situ* and operando techniques, the use of model systems, modelling across the lengthscales (materials to processes) and the use of machine learning. Understanding

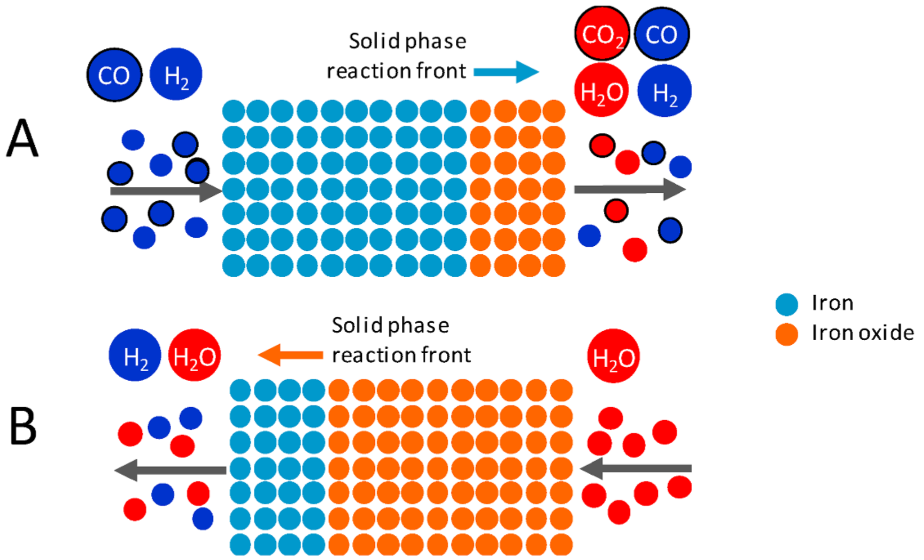

Figure 23. The steam-iron process performed in a fixed bed reactor. In the first stage (A) iron oxide is reduced to iron by a reducing syngas. In the second stage (B) the iron is oxidized by water to produce hydrogen in unreacted water.

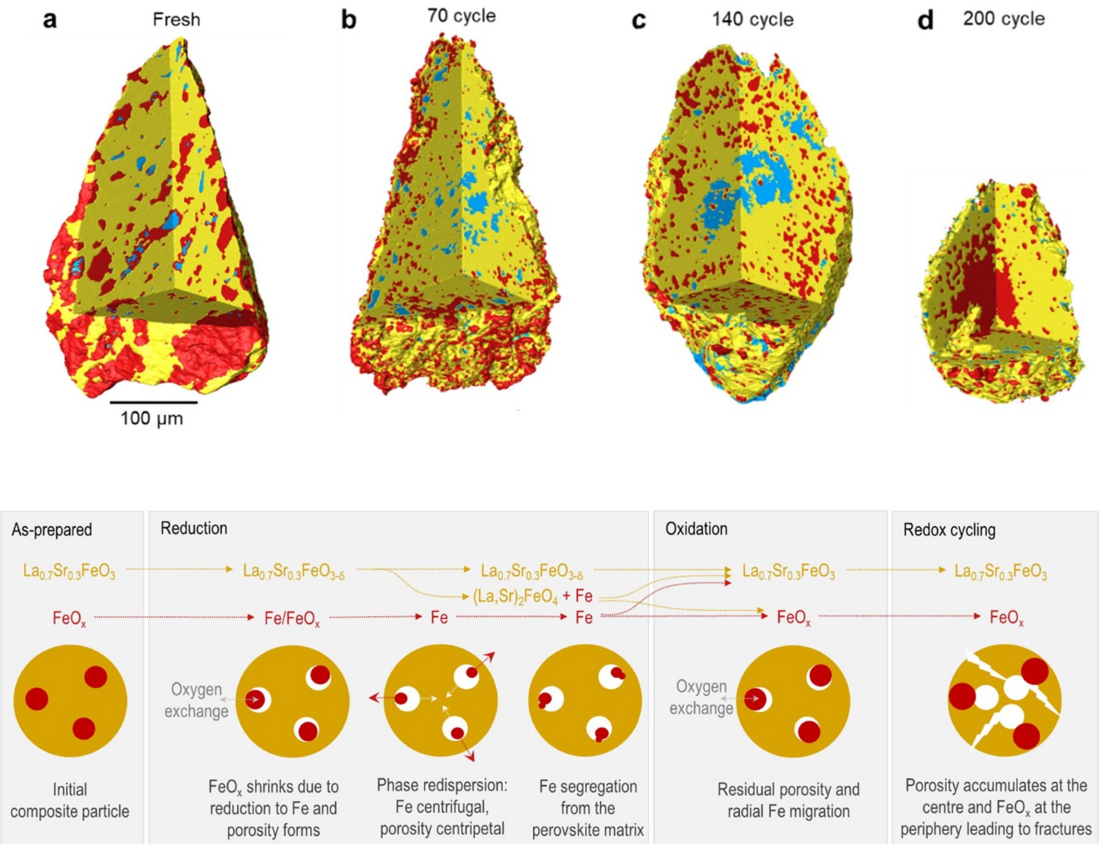

Figure 24. Microstructural evolution of a single composite particle during 200 redox cycles. Phases denoted by red and yellow colours correspond to a majority iron oxide (Fe/FeOx) phase and La$_{0.7}$Sr$_{0.3}$FeO$_3$ while blue denotes porosity. Microstructure and Fe/FeOx particle size and porosity analysis by x-ray CT for a single composite particle after (a) 0, (b) 70, (c) 140 and (d) 200 redox cycles. Below: schematic diagram of the evolution of composite particles during redox cycling. Adapted by permission from Springer Nature Customer Service Centre GmbH: Nature, Scientific Reports [128] © 2020.

the way in which carriers function and evolve during operation will require the development of methods to measure local state of the carrier operando. Synchrotron-based XRD has been used to measure local oxygen content of perovskites [126]. Such techniques, although expensive, could be used more widely. There is also an opportunity to exploit neutron scattering for investigating oxygen content. Tomographic techniques and imaging at different length scales can be used to explore how carriers evolve with time on stream. Recent work (figure 24 [128]) has investigated the evolution of a composite iron oxide-perovskite ($La_{0.7}Sr_{0.3}FeO_3$) particle under redox cycling and shown how iron re-dispersion affects that chemical and physical properties of the carrier.

New methods need to be developed for measuring rates of surface exchange and diffusion *in situ* and operando. It is likely that the kinetic behaviour of carriers, and particularly composite carriers, could be dominated by the role of interfaces. Thus, work with carrier systems where grain boundary composition and density is controlled in model and real structures would be beneficial. The evolution of interfacial properties should be studied. Insights developed should aid design of improved carriers (e.g. composite and core–shell structures [129, 130]) and new synthetic routes for carriers, e.g. the use of exsolution processes [131]. Carrier behaviour should be studied through kinetic work covering model to realistic conditions; there may be a role for high throughput screening.

Perhaps the ultimate scientific advance would be a modelling approach that could fully predict materials behaviour and evolution. We will for some time rely on classical modelling combined with empirical insights into how parameters are affected by e.g. conditions and duration of operation and this will lead to hybrid modelling approaches when combined with property prediction. Interactions with other disciplines such as solid state ionics and catalysis will undoubtedly be important. In the long term data analysis and machine learning may aid carrier design.

12.4. Concluding remarks

There is little doubt that the application of CL promises a future in which we will be able to operate much more efficient chemical conversions with reduced environmental impact. Such ‘unmixed’ reaction processes are thermodynamically distinct from conventional ‘mixed’ reaction processes and these differences will be exploited to deliver radically different and improved processes. However, key to the exploitation of CL is good scientific work in both carrier development and the study of carrier evolution under the demanding conditions of repeated reaction cycling. This will need to be combined with good process engineering in order to develop strategies for reactor operation that capitalize on the benefits of CL while mitigating against loss in carrier performance. In fact, to be most effective, carrier development, process engineering and modelling across the lengthscales must advance as an integrated whole whilst also interacting with related disciplines.

Acknowledgment

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13. Emergent nanoparticles

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13.1. Status

Exsolution, the process by which a solid solution phase unmixes into two separate phases in the solid state, has been known in geology for many decades. However, it was not until the last decade that the utility of such a process for creating new nanostructured materials was revealed. By controlling the defect chemistry of a perovskite lattice containing reducible ions (as a solid solution), and exposing it to reducing environment at temperatures where ions become mobile, those reducible ions emerge (exsolve) into nanoparticles at the surface of the perovskite lattice [132].

As compared to nanoparticles prepared by conventional deposition/assembly methods, emergent nanoparticles form in a single step, simplifying manufacturing, are more uniform in size and distribution and are epitaxially socketed within the surface, exhibiting intriguing new physico-chemical properties such as enhanced carbon deposition and sintering resistance, or strain-enhanced activity [133]. These, along with the possibility to tune size, population, composition or shape, have rendered exsolution as a powerful method for functionalising the surface of perovskites with catalytic activity. Recently, nanoparticles have also been exsolved within the perovskite bulk, causing mutual strain within themselves and the surrounding host lattice, thus opening new opportunities for strain engineering and tuning of bulk transport properties [131].

Exsolution has grown to be not only an alternative route to the decades-long history of deposition/assembly preparation methods, but has set us on a completely new line of thinking in material design, implementation, unlocking unprecedented levels of functionality, reactivity and durability across a range of catalytic and energy conversion applications (figure 25). Emergent nanomaterials promise to deliver exciting opportunities on multiple fronts (figure 26): integrated functionality—creation of systems that combine multiple functional properties tailorable for desired applications (e.g. electron, ion transport, surface activity etc); emergent functionality—due to the diverse, highly correlated phases, interfaces and properties possible, unique new physics and chemistry are expected to be discovered; dynamic, self-adaptive materials—most of the perovskite design is currently static, i.e. the as-prepared structure and function are also final, but exsolution opens the way to create perovskites that can rearrange to desirable structure and function during device integration, operation or can reset to initial structure if degradation occurs over time.

13.2. Current and future challenges

The challenges in achieving these could probably be summarized in four terms: complexity, measurement, modelling and manufacture.

In order to enable exsolution and other additional functional properties, a complex set of design requirements need to be fulfilled, leading to relatively complex perovskite formulations which often combine multiple elements and various defect chemistries. Such diversity has probably lured research into a direction that favours outputting new compositions tailored for a range of applications, in favour of more systematic characterisation of a few, reference or model systems. The lack of a comprehensive structural, compositional, thermodynamic and kinetic data for such reference systems (which control key parameters including particle size, distribution or degree of immersion, thus underpinning physico-chemical properties), together with the difficulties of computationally modelling systems with high concentration of defects/dopants, have made it difficult to establish a well-defined set of rational design principles, which remain largely empirical [134]. The lack of more fundamental property investigation has also probably precluded exsolution from yet reaching other fields like physics where, e.g. magnetic properties could be of interest.

While exsolution is a relatively simple, single-step treatment, the fundamental transport processes that make it happen are quite complex, involving lattice oxygen removal and subsequent electron doping, nanoparticle nucleation and growth and diffusion of oxide ions and cations across the surface and bulk. Some of these processes, may not only limit exsolution but also raise challenges for understanding, monitoring and controlling it. For example, perovskite surface segregation/reorganisation limit cation transport to the surface, trapping ions in the bulk thus limiting the amount of particles that can be formed at the surface. Ion diffusion within the bulk itself can also limit the rate and extent of exsolution leading to the necessity of high temperatures or long durations.

Such a complex overlay of phenomena, in the presence of many point defects and emerging interfaces has not only made it difficult to model computationally but has also difficult to monitor and characterize in real time since a range of techniques would be required to probe structural changes across length-scales and time-scales, in the bulk and at the surface.

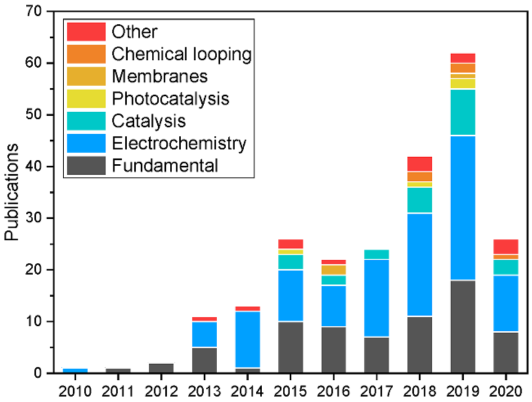

Figure 25. Publications using 'exsolution' as keyword over the last decade. Curated by using Google Scholar and 'Publish or Perish' software by Harzing (2007), available from https://harzing.com/resources/publish-or-perish. This is not an exhaustive list and only contains about 200 journal papers. 'Other' includes sensor, thermoelectric and magnetic applications.

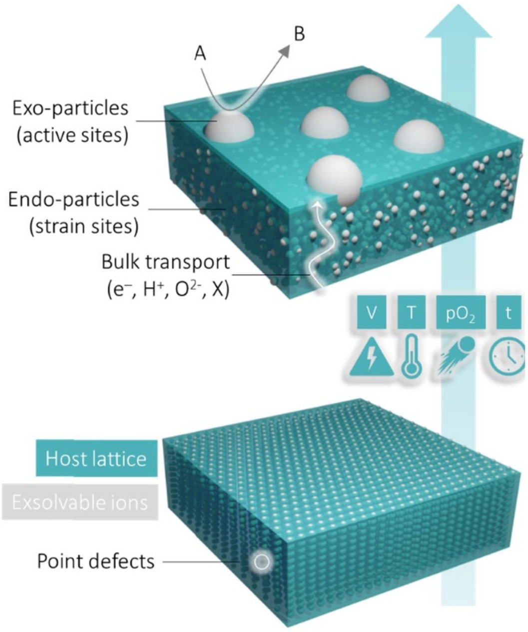

Figure 26. Schematic depiction of the exsolution concept, illustrating factors involved in control and functionality.

13.3. Advances in science and technology to meet challenges

There are probably two different sets of parameters to design, control and investigate the structure and function of exsolved materials: intrinsic (related to the material) and extrinsic (related to the conditions in which the material is exposed to trigger exsolution).

Many intrinsic parameters are yet to be explored, including different perovskite-related crystal structures or defect chemistries, less-explored elements, or different anion sublattice (e.g. halides, nitrides or oxycarbides) [141–143]. These could enable new classes of catalytic materials for photo/electro catalysis, help alleviate surface and bulk transport limitations, lowering the exsolution temperature and enabling new opportunities in electrochemical applications at near-ambient conditions. Diversifying the microstructures in which the crystal lattices are formed and deployed is also key, investigating higher surface area powders, thin films or hierarchically structured perovskites. Finally, it is imperative to develop synthetic routes that allow the controlled preparation of such complex perovskite lattices and microstructures at lab and pilot scale for transition to industry.

In terms of extrinsic parameters, we already know that chemical or electrochemical driving forces can trigger exsolution, but other means (e.g. light-driven) should be explored to realize self-adaptive capabilities for device implementation [47, 135, 138]. We also know that reduction temperature and time control particle size and population, but more work is needed to rationalize the effect, ultimately enabling us to exsolve single atoms, one of the ultimate frontiers in efficient catalyst design and function. Lastly, there is evidence that the pO_2 and the nature of the reducing atmosphere dictates nanoparticle shape and composition, but more work is needed to control this effect [139].

The combination of intrinsic and extrinsic parameters makes for virtually infinite structural and functional diversity and understanding the interplay and overlay of these will be key in discovering new, emergent functionality. To monitor and characterize these, comprehensive, correlated techniques will have to be more routinely employed or developed. A range of x-ray techniques, particularly at synchrotron scale, would be highly desirable: x-ray photoelectron spectroscopy (surface), diffraction (bulk phase composition and crystal arrangement), absorption spectroscopy (ion oxidation state and coordination environment), computed tomography (microstructure and phase distribution). Ideally these would be coupled with physical property measurement such as electrical, electrochemical and magnetic measurements. Such a correlated data set could also greatly aid in the computational efforts to rationalize these materials.

13.4. Concluding remarks

Exsolved emergent nanomaterials have already revolutionized the way we think about material design and implementation across multiple fields including catalysis and energy conversion. Undoubtedly the field will continue to grow as this approach and the wealth of multifunctionality it brings continues to be adopted by research groups across different fields. While the complexity of formulation, rationalisation and underpinning fundamental processes remain challenging, they also breathe new life in the world of perovskites promising to deliver smarter, self-adaptive materials with emergent properties and providing motivation to develop advanced correlated techniques.

14. Li-perovskites: interest and future prospects

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14.1. Status

Li-batteries have led the revolution of device-systems to power portable electronics or electrical vehicles and to storage energy from renewable sources. Higher energy density and improvements on safety and cycling life are expected on all-solid-state-batteries (ASSBs) based in inorganic solid electrolytes [140]. Li-perovskites are among the most promising electrolytes for oxide and sulfide ASSBs. Outstanding high Li-conductivity at room temperature in a perovskite was first reported in 1993 in $La_{0.5}Li_{0.34}TiO_{2.94}$ ($\sigma_{295K} \sim 1 \times 10^{-3}$ S cm^{-1}) [141]. This discovery kicked off an intense search for establishing composition-structure-properties relationships in this type of perovskite-oxides. The study of the stoichiometric range of the $La_{(2/3)-x}Li_{3x}TiO_3$ system and its thermal stability was crucial to obtain single phases [142] and full determination solving the crystal structure of these Li-perovskites [143]. The aim of increasing Li-conductivity guided the study of other La/Li titanates with the perovskite structure and so to optimize composition and properties, in such a way that the highest conductivity reported so far has been in the oxide with composition $La_{0.56}Li_{0.36}Ti_{0.97}Al_{0.03}O_3$ ($\sigma_{295K} = 2.95 \times 10^{-3}$ S cm^{-1}) [144]. Yet, despite the excellent Li-conducting properties of these perovskites, La/Li titanates face two major issues: high resistance associated to grain boundaries in polycrystalline ceramics, which can decrease the total conductivity more than one order of magnitude, and a narrow electrochemical window, since these titanates are not electrochemically stable below 1.8 V vs. Li due to the reduction of Ti^{4+} to Ti^{3+}. Nonetheless, perovskite oxides present some advantages in comparison with the other studied Li solid electrolytes such as higher chemical stability in air and wider electrochemical window than $Li_{10}GeP_2S_{12}$ and higher resistance towards humidity, although lower electrochemical stability than Li-garnets [140]. Interestingly enough, the high resistance and capacitance associated to the grain boundaries, which limits the application of these ceramics as electrolytes, results in a 'giant' dielectric permittivity making these Li-perovskites to behave as barrier layer capacitors [145]. Despite the aforementioned inconveniences, the properties of Li-perovskites still place these materials among the most valuable solid electrolytes for ASSBs, figure 27.

14.2. Current and future challenges

Widening the electrochemical window and eliminating grain boundaries are the main challenges for the practical implementation of Li-perovskites as electrolytes in ASSBs. Replacement of Ti by other non-reducible metal atoms is essential to increase the operating voltage range. In this context, the pioneering work in the $La_{(1/3)-x}Li_{3x}NbO_3$ system [146] led to interesting conclusions that started new research on Li-perovskites with transition metals of the second and third rows of the Periodic Table. In addition to a wider electrochemical window, the niobates reduces grain boundary effects, although the total conductivity is significantly lower than the bulk conductivity of the titanates. The decreasing of the bulk conductivity of these niobates seems to be related to the higher amount of A-cation vacancies in the system; these are concentrated in completely empty (001)-layers limiting the conduction within the La/Li/vacancy-layers [147]. Improvements on Li-conductivity and operating voltage range have, nevertheless, been achieved in tantalates and niobates doped with Zr and Hf; in particular in the $Li_{3/8}Sr_{7/16}Hf_{1/4}Ta_{3/4}O_3$ perovskite, which presents a total conductivity of 3.8×10^{-4} S cm^{-1} at room temperature and is stable above 1.4 V vs Li [148]. Therefore, synthesizing Li-perovskites with the appropriate atoms to be electrochemically stable, with the optimum composition to achieve the highest ionic conductivity, that seems to be associated to around 8 mol% of vacancies within the A positions [144], and minimizing grain boundary effects, although grain boundary resistances are overcome for the case of thin film processing [140], are the main issues to be addressed currently. Besides, Li-perovskites, like other solid electrolytes [149], face the challenges of electrode/electrolyte interface stabilization and physical contact. Formation of high ion-resistive and/or electron-conducting phases at the interfaces might avert a satisfactory battery performance, like for sure do a poor physical contact or mechanical stress.

14.3. Advances in science and technology to meet challenges

Though rational thinking and search are the essential tools to advance Science, the development of characterization techniques has allowed discovering and dealing with research problems that were not possible to solve decades ago. In this sense, in addition to advanced methods on powder x-ray-including synchrotron-, neutron and electron diffraction, and high resolution transmission electron microscopy

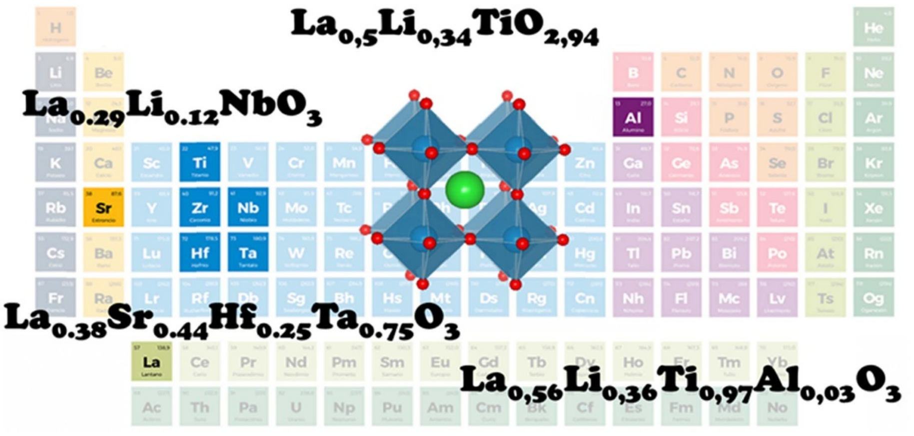

Figure 27. Li-perovskites with high bulk Li-ion conductivity.

(HRTEM), that have strongly contributed to elucidate the crystal structure of Li-perovskites for the understanding of their Li-conducting properties [142, 143] and to study their defect chemistry, complex structures have been imaged with atomic resolution by scanning-TEM [147], which is a technique clearly called to play a significant role in the study of the electrode/electrolyte interfaces. Worth noting, nuclear magnetic resonance (NMR) is, also, a powerful tool to study the local structure and diffusion mechanisms in solid inorganic Li-electrolytes. In addition, the development of experimental setups such as '*in situ*' HRTEM, neutron diffraction and NMR to identify phase formation and evolution taking place during battery operation are obviously highly interesting. On the other hand, computational methods have demonstrated strong capacity to design new Li-materials. And last, but not least, development of synthesis and processing routes will certainly help to optimize particle size and morphology, densification of materials, etc for the best battery performance.

14.4. Concluding remarks

Research on Li-perovskites is currently highly encouraged owing to their potential applications as solid electrolytes in ASSBs. The excellent bulk ionic conductivity of the titanate-oxides has not yet been surpassed by other Li-perovskite systems. However, their relatively narrow electrochemical window has moved the interest into Li-perovskites with transition metals of the second and third rows of the periodic table. Intensive research in the field, will eventually achieve to overcome major challenges and the successful development of optimum Li-perovskites for applications.

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Data availability statement

No new data were created or analysed in this study.

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