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Amini-review on proton conduction of BaZrO3-based perovskite electrolytes

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ABSTRACT
Proton conducting ceramics show promise in fuel cells, electrolyzers, permeation membranes,sensor applications, and membrane reactors. Among several types of materials that exhibit protonconduction, perovskite oxides show high proton conductivity at intermediate temperatures,presenting potential benefits for long-term use and lower costs for energy applications. Dopedbarium zirconate, $BaZrO_3$, isamaterialthathasshownhigh   proton conductivitywithencouragingchemicalstability.Therefore,itisconsideredapromisingmaterialespeciallyfor proton-conducting solid oxide electrochemical cells. Although the proton conduction of dopedBaZrO$_3$ has been extensively   characterized,   the   specific   phenomena   behind   its   proton conductionarenotfullyunderstood.Onlyrecentlyhavespecializedtechniquesandcomputationaltoolsbeguntoelucidat ethephenomenathatdeterminetheconductionpropertiesofthematerial.Inthisminireview,anevaluationofthefactorsaff ectingtheprotonconductivityofdopedBaZrO$_3$perovskitesandthephenomenagoverningvariationsinprotonconcentrat ionandmobilityarepresented.
Special   attention   is   given   to   proton   interactions   with   dopants   and   their   resulting   effect onhydrationandtransportproperties.Technicalstrategiesareprovidedtogivesomeguidanceonthedevelopmentofproto nicceramicsinenergyconversionapplications.

Keywords:protonconductor,perovskiteceramics,hydrationthermodynamics,protonconcentration,protontrapping,s olidoxidecells

INTRODUCTION

The interest in proton-conducting ceramics has continuously grown since the 1980s when protonconductionwasfirstobservedindopedSrCeO$_3$o xidesathightemperatures($>600^{\circ}C$)inahumidifiedatm osphere[1,2].Lateron,somenewmaterialssuchasnobi ates[3],tantalates[3],perovskites,and disorderedperovskites[4,5],wereshowntoexhibitprot onconductivity.Eachmaterialfamilydemonstratedits own special characteristics, requiring a deeper understanding of each to optimize proton conduction for agiven application. The applications of proton-conducting ceramics are diverse: sensors, hydrogen separationmembranes, fuel cells, steam electrolyzers, and membrane reactors [6–11]. In particular, there has beensignificant recent interest in their use in solid oxide electrolysis cells (SOECs)   for   hydrogen   production. TheSOECsbasedonproton-conductingelectrolytes,theproton-conductingSOECs(p-SOECs),candeliverpurehydrogen with some critical advantages over conventional oxide-ion conducting SOECs: reduced operatingtemperature, absence of nickel oxidation, and dry hydrogen production without   the   need   for   furtherseparation[12–

19].Additionally,withthehighprotonconductivityoft heseconductorsandtheoptimizationofcompositionan dfabrication,theelectrolysiscurrentdensityhasbeenin creasinglyimproved.Still,   the   development   of electrolytes remains challenging due to a restrained total   conductivity, chemicalstability,andtheelectronicconductionunder gasconditionswhichcanreducecurrentefficiency

[1,16,17,20,21].Furthermore,considerationonpotent ialelectronicleakageduringelectrolysisisoperation,as found in recent works [16, 17, 21, 22], has become an additional concern that can be addressed byrevealing the mechanism of the electronic conduction and developing new protonic ceramics. To betteraddress these technical concerns, it is important to understand the underlying mechanism of protonconductiontopromoteinnovationsinelectrolyt ecompositionforpracticaloperationatlowertemperatu res.
Proton conductionisatemperature-activatedprocess andisobservedinwater-containingatmospheresasafunctionofgasatmosphere .Equation(1)showstherelationshipofprotonconducti vity($\sigma_{OH}\bullet,Sm^{-1}$)

withtemperaturefollowing anArrheniustype dependence,

$$\sigma_{OH_o^\bullet} = \sigma^* \exp\left(-\frac{E_a}{kT}\right) \quad (1)$$

where $\sigma^*_{OH_o^\bullet}$ isthepre-exponentialfactordescribingprotonconductivity(Sm^{-1}),$E_a$istheactivationenergy forprotonconduction(eV),$k$istheBoltzmannconstant, and Tisthetemperature(K).

Amongseveralproton-conductingperovskitesdevelopedinthepastdecades,dopedBaCeO$_3$andBaZrO$_3$have shown the most promising application potential due to their high proton conductivity, chemicalstability,andfabricationfeasibility[5,16,23–27].PerovskitesystemscontainingCe(BaCeO$_3$and BaCe$_{1-x}$Zr$_x$O$_3$)exhibithighconductivity[23,24,28].However,theirlowchemicalstabilityinsteamandCO$_2$gasisasubjectofconcern[29–33].Incontrast,severalstudieshaveshownthatBaZrO$_3$isstablein steam and CO$_2$ and does not form BaCO$_3$ and Ba(OH)$_2$ phases [18, 34–38], unlike BaCeO$_3$ andBaCe$_{1-x}$Zr$_x$O$_3$ systems [29, 32, 39, 40]. Therefore, doped BaZrO$_3$ is a suitable material for p-SOECsapplications andwillbethesubjectofthisminireviewtoillustratethe protonconduction phenomena.

BaZrO$_3$dopedwithY,Yb,In,Sc,Gd,Nd,Sm,etchavebeen extensivelyinvestigatedaselectrolytesthatdemonstrate considerableprotonconductivitywithoptimizeddopantelementandconcentration[5,25,26].Several researchers have reported that the dopant and its concentration can considerably affect the protonconductivityofsuchmaterials[5,25,26].Moreover,correlationsbetweendopantatomicradius[25,26] andelectronegativity [41] with hydration energies and conductivities had been reported. Among doped BaZrO$_3$compounds,20%Y-dopedBaZrO$_3$ hasthehighestconductivitytodate[5,25,42].However, thereisalackofcomprehensive studies of doped BaZrO$_3$ to characterize the differences between proton concentration andmobility with temperature and gas conditions. Meanwhile the pursuit of other possible compositions basedonBaZrO$_3$perovskitesisstillongoingtoachievehigherconductivity.
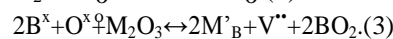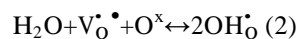
This mini review will present the fundamental effects of defects location in material hydration andproton conduction. First,hydration thermodynamicsfor dopedBaZrO$_3$materialsandtheeffectof dopingon hydration and proton defect formation are reviewed. Second, proton localization in the lattice,particularlywithrespecttooxygen vacanciesanddopant atoms, andtheeffectonproton concentration andmobility are presented in the context of defect associations and proton trapping phenomena. Finally, wepresent theimplications of electronic conduction andstrategiesandfuture directions for further studies ofproton-conductingmaterials.

Thermodynamicsofhydrationinprotonconductors
Thestudyofhydrationthermodynamicsisimportantfor thecharacterizationofnewproton-conductingmaterials because hydrationability determines protonconcentrationunderspecific gas conditionsand temperatures.Protonsareincorporatedintothematerialthroughthehydrationofoxygenvacancies($V_O^{\bullet\bullet}$), asshowninequation(2).TheoxygenvacanciesareusuallycreatedbydopingtheB-siteoftheperovskite (ABO$_3$)withatrivalentelement(M)(equation(3)),andtheirconcentrationcorrespondstohalfthedopantconcentration. The hydration of oxygen vacancies in equation (2) is key as it determines the protonconcentration([OH$_O^\bullet$],%mol)ofthematerial,whichisafunctionoftemperature,andunderincomplete hydration,afunctionofwaterpartialpressure(P_{H2O})

$$H_2O+V_O^{\bullet\bullet}+O_O^x \leftrightarrow 2OH_O^\bullet \quad (2)$$
$$2B^x+O_O^x+M_2O_3 \leftrightarrow 2M'_B+V_O^{\bullet\bullet}+2BO_2. \quad (3)$$

Favorable hydration thermodynamics can be used as a guide for proton conduction as it is related to protonconcentration asfunction of temperature. In thissection, thebasicsof thehydration thermodynamics arereviewedbyadiscussionabouttheincompletehydrationregime.

**Table1.** ΔH_{hyd} and ΔS_{hyd} of various doped $BaZrO_3$.

Material	ΔH_{hyd} (kJmol^{-1})		ΔS_{hyd} (Jmol^{-1}K^{-1})		Reference
$BaZr_{0.9}Y_{0.1}O_{3-\delta}$	−79.4		−88.8		[5]
$BaZr_{0.8}Y_{0.2}O_{3-\delta}$		−93.3		−103.2	[5]
$BaZr_{0.8}Y_{0.2}O_{3-\delta}$		−22		−39	[50]
$BaZr_{0.7}Y_{0.3}O_{3-\delta}$		−26		−44	[50]
$BaZr_{0.6}Y_{0.4}O_{3-\delta}$		−26		−41	[50]
$BaZr_{0.9}Sc_{0.1}O_{3-\delta}$		−119.4		−124.9	[5]
$BaZr_{0.8}Sc_{0.2}O_{3-\delta}$		−96		−104	[51]
$BaZr_{0.9}Gd_{0.1}O_{3-\delta}$		−66.1		−85.9	[5]
$BaZr_{0.9}In_{0.1}O_{3-\delta}$		−66.6		−90.2	[5]
$BaZr_{0.9}In_{0.1}O_{3-\delta}$		−67		−90	[52]
$BaZr_{0.5}In_{0.5}O_{3-\delta}$		−60		−95	[52]
$BaZr_{0.25}In_{0.75}O_{3-\delta}$		−74		−109	[52]

The thermodynamics of the hydration reaction, equation(2), determines the proton concentration of the material as a function of temperature. The formation of the proton defect is governed by the equilibrium constant of the hydration reaction (K_{hyd}), equation(4)

$$[OH_O^\bullet]^2$$

$$K_{hyd} = \frac{P}{[V_O^{\bullet\bullet}][O_O^x]}$$

(4)

$$H_2O$$
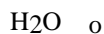
K_{hyd} is then related to the Gibbs free energy of hydration(ΔG_{hyd}) according to equation(5), while ΔG_{hyd} is related to the enthalpy(ΔH_{hyd}) and entropy (ΔS_{hyd}) of hydration according to equation (6). Therefore, ΔH_{hyd} and ΔS_{hyd} can be calculated from knowing K_{hyd} as a function of temperature through the Van't Hoff equation, as shown in equation(7)

$$\Delta G_{hyd} = -RT\ln K_{hyd}$$

(5)

$$\Delta G_{hyd} = \Delta H_{hyd} - T\Delta S_{hyd}$$

(6)

$$\ln K_{hyd} = -\frac{\Delta H_{hyd}}{RT} + \frac{\Delta S_{hyd}}{R}.$$

(7)

Favorable hydration thermodynamics is often characterized by a highly exothermic ΔH_{hyd}, a less negative ΔS_{hyd}, and a negative ΔG_{hyd}. Materials with more exothermic heats of hydration favor higher degrees of hydration as temperature rises[43]. The entropic impact of hydration is related to lattice ordering due to proton incorporation[5], which results in lattice expansion upon hydration and includes configuration and vibrational contributions[44]. In general, a less negative value of ΔS_{hyd} usually results in greater retention of protons

at higher temperatures [44,45]. Studies of doped $BaZrO_3$ hydration thermodynamics have correlated ΔH_{hyd} with the electronegativity of the dopant and tolerance factor of the material[41,46,47]. As the tolerance factor and electronegativity of the dopant decreases, $\De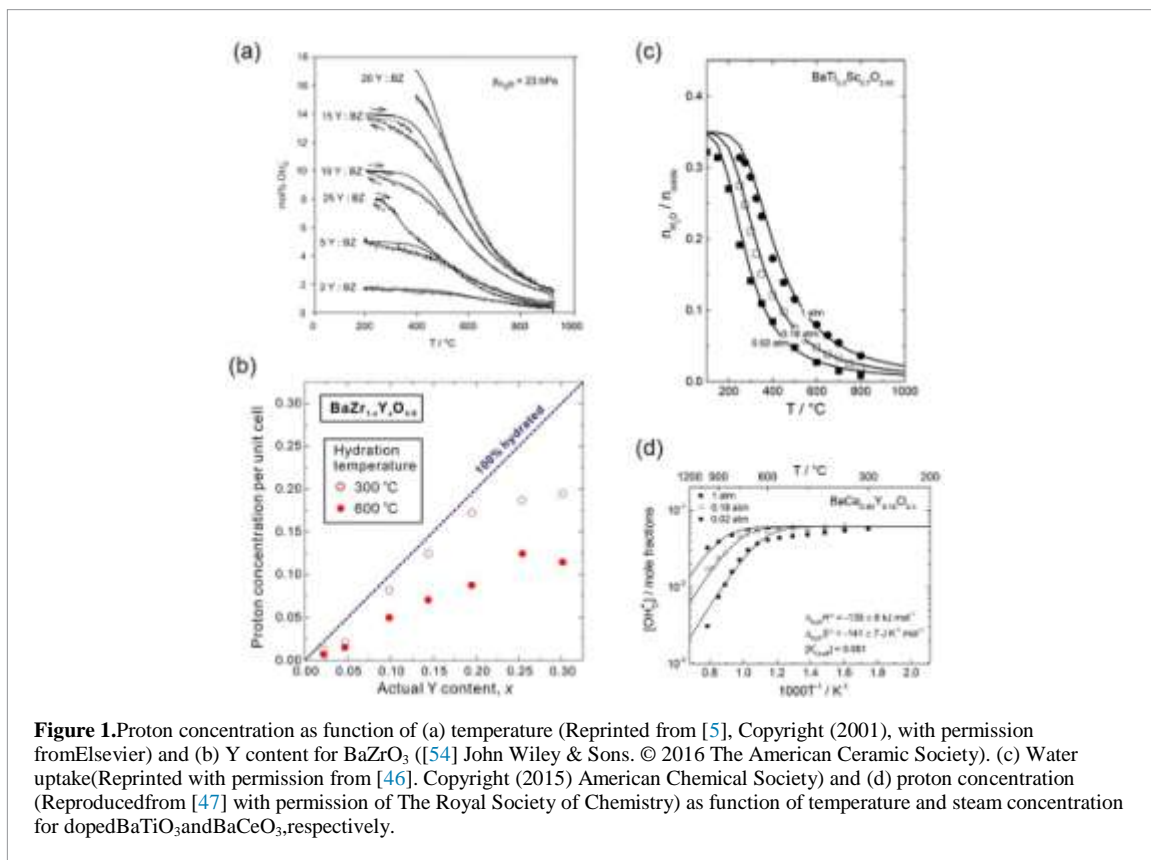lta H_{hyd}$ tends to be more exothermic [47]. The effects of the dopant and its concentration on ΔH_{hyd} and ΔS_{hyd} are summarized in table1. The values of ΔH_{hyd} and ΔS_{hyd} are dependent on the dopant, decreasing in hydration energy as follows: Gd>In>Y, with Sc-doped $BaZrO_3$ exhibiting the most favorable ΔH_{hyd}. However, ΔH_{hyd} and ΔS_{hyd} do not show any clear dependence on dopant concentration. Differences in the values of the hydration energy between references for a same material correspond to possible non-linear hydration isobars in all temperature ranges ascribed to defect interactions[48,49] or to the formation of electronic species[50].

An important feature that results from studying the hydration of a material is the characterization of proton concentration with temperature. The hydration limit of doped $BaZrO_3$ frequently corresponds to the theoretical level of the dopant concentration[M]. Proton concentration as a function of temperature has been reported for numerous doped $BaZrO_3$ where the proton concentration reaches a maximum value at a low temperature and follows a decreasing trend with increasing temperature, as shown in figure 1(a). Proton concentration is normally studied through thermogravimetric analysis by correlating the weight increase from water uptake to the proton concentration, usually while studying hydration thermodynamics. Nuclear magnetic resonance(NMR)[53] has also been used to quantify the proton concentration. The application of these materials for p-SOECs requires operating temperatures in the range of 400 °C–600 °C, i.e. in the incomplete hydration regime, as seen in figures 1(a) and(b). A thoughtful characterization of the incomplete

Figure 1. Proton concentration as function of (a) temperature (Reprinted from [5], Copyright (2001), with permission fromElsevier) and (b) Y content for BaZrO₃ ([54] John Wiley & Sons. © 2016 The American Ceramic Society). (c) Water uptake(Reprinted with permission from [46]. Copyright (2015) American Chemical Society) and (d) proton concentration (Reproducedfrom [47] with permission of The Royal Society of Chemistry) as function of temperature and steam concentration for dopedBaTiO₃andBaCeO₃,respectively.

hydration regime becomes essential to determine optimum doping concentrations. However, there are notmany studies exploring this relationship. Moreover, in the incomplete hydration regime, protonconcentration is a function of steam concentration [46, 47], as seen in figures 1(c) and (d) for otherperovskites. Figures 1(c) and (d) suggest that proton concentration increases as steam concentrationincreases,althoughtheeffectismoresignificantinthelowsteamconcentrationregion.FuturestudiesontheprotonconcentrationindopedBaZrO₃asafunctionofsteamconcentrationandtemperatureshouldrevealthedynamicofmaterialhydration.

It is worth pointing out that BaZrO₃-based electrolytes are refractory materials that require highsintering temperatures.Toreducethe sintering temperatureandimprovedensification,sintering aids (NiO[55–57],ZnO[58–61],CuO[55,62],CaO[63],BaO–B₂O₃[64],BaY₂NiO₅[65],etc)havebeenused to facilitate densification by introducing a liquid phase for grain growth [66]. However, recent studies haveshown that sintering aids have negative impact on the proton concentration [67–69], thus reducingconductivity.Inaddition,thesinteringaidsfav

orthedetrimentalformationofBa-vacancies[67,68]andtheformation of undesired secondary phases in Y-doped BaZrO₃ [69–71]. Therefore, it is important tominimize the use of sintering aids or adopt other strategies for the material densification to suppress theimpactofsinteringaidsontheconductivity.

Based on K_{hyd} and the hydration energies, lower temperatures and higher steam concentrations arefavorable for the hydration of oxygen vacancies. A higher concentration of oxygen vacancies increases theproton concentration. The doping of the Zr-site is the most common strategy to create oxygen vacancies butBa-site doping has also been explored [72–74]. The oxidizing character of the steam carrier gas is anotherimportant factor to consider during hydration as the oxidation of oxygen vacancies at certain experimentalconditions[75,76]coulddecreasetheeffectiveconcentrationofoxygenvacanciesthatcanbehydrated.Theeffects of oxygen vacancies and dopant atoms in the material hydration will be discussed in the followingsections.

Effectofoxygenvacanciesanddefectsassociationonhydrationandprotonconcentration

The location of oxygen vacancies and the extent of defect association are a representation of the chemicalenvironmentdifferencescausedbydopantsa

ndtheirconcentration.Thesedifferencesaremanifeste dinthehydrationenergiesand,consequently,inprotonc oncentration.Whileithasbeensuggestedthatoxygen
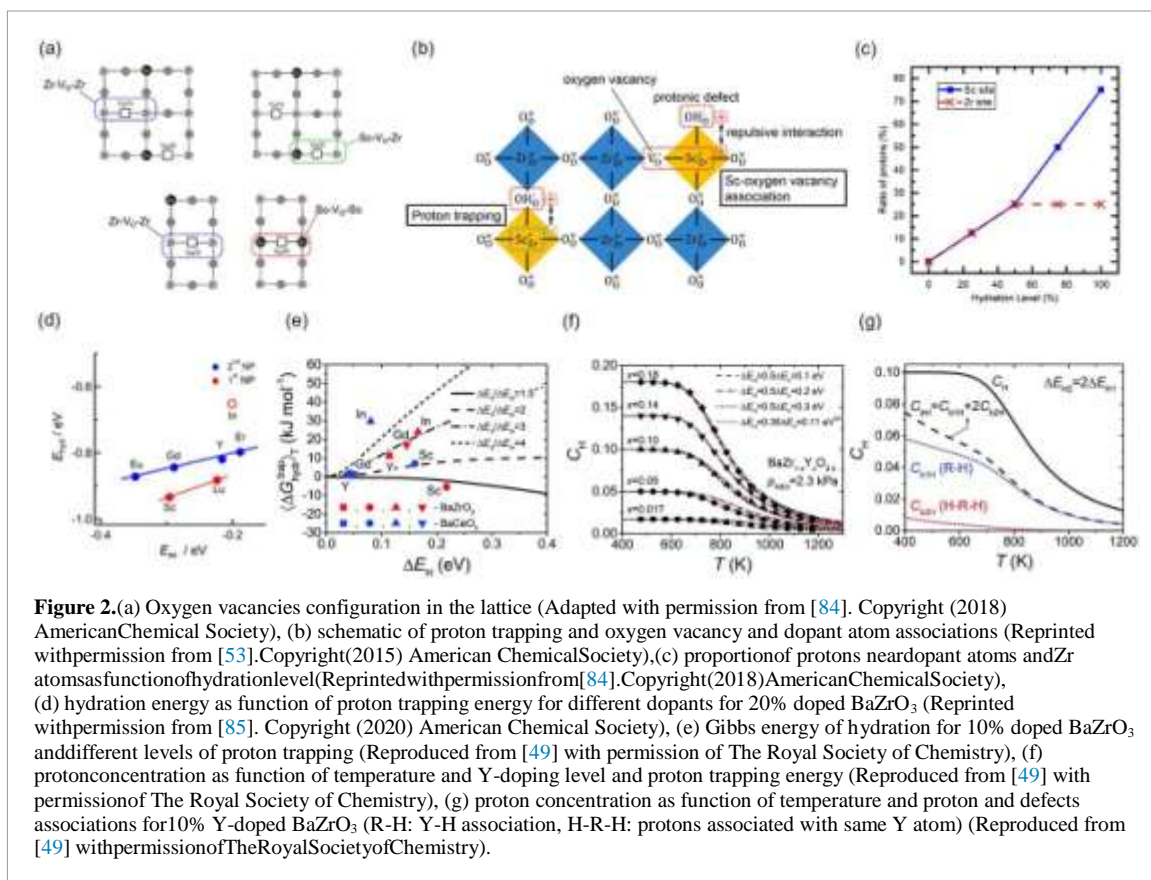

Figure 2.(a) Oxygen vacancies configuration in the lattice (Adapted with permission from [84]. Copyright (2018) AmericanChemical Society), (b) schematic of proton trapping and oxygen vacancy and dopant atom associations (Reprinted withpermission from [53].Copyright(2015) American ChemicalSociety),(c) proportionof protons neardopant atoms andZr atomsasfunctionofhydrationlevel(Reprintedwithpermissionfrom[84].Copyright(2018)AmericanChemicalSociety), (d) hydration energy as function of proton trapping energy for different dopants for 20% doped BaZrO$_3$ (Reprinted withpermission from [85]. Copyright (2020) American Chemical Society), (e) Gibbs energy of hydration for 10% doped BaZrO$_3$ anddifferent levels of proton trapping (Reproduced from [49] with permission of The Royal Society of Chemistry), (f) protonconcentration as function of temperature and Y-doping level and proton trapping energy (Reproduced from [49] with permissionof The Royal Society of Chemistry), (g) proton concentration as function of temperature and proton and defects associations for10% Y-doped BaZrO$_3$ (R-H: Y-H association, H-R-H: protons associated with same Y atom) (Reproduced from [49] withpermissionofTheRoyalSocietyofChemistry).

vacancies tend to form in the vicinity of dopant atoms [53, 77], different configurations of oxygen vacanciescanexist.Severalworkshavesuccessfullypro bedthelocalizationofoxygenvacanciesandprotonsatd ifferentconfigurations in doped BaZrO$_3$ by using specialized techniques such as neutron spin-echo [78], x-rayabsorption spectroscopy [52], quasielastic neutron scattering [79, 80], Fourier transform infraredspectroscopy [81–83], and NMR [53, 84]. Some of those configurations correspond to oxygen vacancies inbetweenZratoms(Zr−V$^{..}$−Zr),betweenaZratomand adopantatom(Zr−V$^{..}$−M),andinbetween dopant atoms (M − V$^{..}$− M) [84], as represented schematically in figure 2(a). The distribution of suchconfigurations can be a function of the dopant atom and its concentration as a result of charge compensationduringtheformationof oxygen vacancies(equation (3)).Ontheother hand,positivelychargedprotonsandoxygen vacancies can associate with negatively charged dopant atoms [53], as seen in figure 2(b), for whichthe extent of such associations is a function of the dopant [77]. In this section, the oxygen

vacancy locationand defect associations will be used to discuss the hydration energy and proton concentration of dopedBaZrO$_3$.
Thelocationofoxygenvacanciesbeforetheirhydration hasanimpactonhydrationenergy.
Consequently, oxygen vacancies near dopant atoms can be part of defect associations that can modify thehydrationthermodynamicsandthetreatmentofexp erimentaldataaboutthematerialhydration[48,49].Co mputational works have shown that the hydration energy of each configuration is different, suggestingthat the experimental hydration energies are an average of all the different hydration energies for all theoxygen vacancy configurations [84, 86]. Additionally, some attempts to link the extent of hydration to thelocation of oxygen vacancies have been made by relating the stability of oxygen vacancies with theirhydration abilities [84]. For example, density functional theory (DFT) of Sc-doped BaZrO$_3$ showed that thestability of oxygen vacancies depends on its location, being more stable near Sc atoms in comparison withoxygen vacancies near Zr atoms [84]. Consequently, the less stable oxygen vacancies are

easier to hydratethanthemorestableoxygenvacancies[84,87]. Thisissignificantasthehydrationofsomeoxygenvacan ciescouldresultinprotonsinprotontrappingpositions. However,aSc-NMRstudyonthehydrationof Sc-doped BaZrO$_3$ revealed that at low proton concentrations, i.e. low material hydration due to hightemperature, the protons were located equally near the Sc and Zr atoms [53, 84]. But as the protonconcentrationincreased,i.e.amaterialhydratio nincreasedbylowtemperatures,mostoftheprotonswer elocatednearSc[53,84],asseeninfigure2(c).

The association of a proton with a dopant atom is referred to as proton trapping. DFT studies havecorrelated hydration energy with proton trapping energy for different dopants in BaZrO$_3$. The resultssuggested that high proton trapping energy led to more exothermic hydration energies [85], as shown infigure 2(d). However, another DFT study suggested that proton trapping can enhance or inhibit thehydrationofthematerial[49],ascanbeobservedfro mfigure2(e)wheretheGibbsfreeenergyofhydrationis presentedasafunction of theprotonassociation energies.Such boundariesdepend on thedopant anditsconcentration, as well as the trapping energy for the proton and for the oxygen vacancies with the dopant[49].Asshowninfigures2(d)and(e),asdefectas sociationsaffecthydrationequilibrium,failingtoinclu dethese associations in the data analysis of hydration measurements could affect the calculation of protonconcentrations [48, 49, 85, 88]. As seen in figure 2(f), at higher doping concentration for Y-doped BaZrO$_3$,theprotonconcentrationdoesnotreachthetheo reticalvaluesatthelowtemperatureregion[49]. Additionally, the overall proton concentration could be divided between the un-associated protons andtrapped protons [49], as seen in figure 2(g). The effect of trapped protons and unassociated protons onprotonconductionwillbereviewednext.Nonethele s,thecomplexityaddedbydefectassociationonprotonc oncentrationmustbeunderstoodasthesearchfortheopt imumdopantanddopingconcentrationofBaZrO$_3$conti nues.

Protonconductioninsolidoxides
It is well recognized that protons diffuse through solid oxides by the Grotthuss mechanism. Proton diffusioninvolves the reorientation of a proton towards a neighboring oxygen atom and the jump of the protontowards the neighboring oxygen atom [41, 89], as shown in figure 3(a). The proton jump step is mostlyconsidered as the rate limiting step [41, 89]. Due to the nature of the Grotthuss mechanism, thecharacteristicsoftheO–

Hbondbecomeimportantintheunderstandingofproto nconductioninperovskites. The O–H bond can be stretched, shortened, andreoriented due to the atoms around it, changingin strength accordingly [82]. Normally, when the O–H bond is stronger, the rate of reorientation decreasesandproton transfer increases [82]. Oxygen vacanciesanddopantatoms canmodifytheO–Hbond strength.For example, it was reported that as the oxygen vacancies and dopant atoms influence a repulsive andattractive force around the proton due to their positive and negative charge, respectively, the proton tiltstowardsaneighboringoxygenandhencestrongerO – Hbondsarecreated[82].Theoveralleffectisobservedi n the increase in the proton jump step at the expense of slowing the reorientation step [41, 82], modifyingthe activation energy for proton diffusion. Moreover, the B–H interaction can also contribute to theactivation energy of proton diffusion as the repulsive interaction between a proton and the host atom Binhibitstheformation of alinearO–Hbond, resultinginan increase of activation energyfor proton transfer[41, 45, 90]. The B–H interaction can be modified by doping resulting in changes in the basicity of theoxygenatomsandintheactivationenergyforproton diffusion[41,90].
Proton diffusion from the surface to the bulk of the material could represent an important energy barrier,as suggested by DFT studies in proton conductor oxides [87, 91]. As seen in figure 3(b), the energy barriersfortheinitialprotonjump(IandTinfigure3(b))a rehigherthantheenergybarrierforprotonjumpsawayfr om the surface [91]. Additionally, the study of the material surface and its space charge region is relevantfor the study of the hydration process [87, 92]. Proton diffusion into the bulk requires the counter diffusionof oxygen vacancies from the bulk to the surface, and therefore, the predicted depletion or segregation ofoxygenvacancies(figure3(c))couldincreasetheener gybarriersforprotondiffusionfromthesurfacetothebul k ofthematerial.Thoroughstudiesabouttheenergybarri ersonprotondiffusionfrom thesurfacetothebulk in doped BaZrO$_3$ could help explain the differences in conductivity observed experimentally fordifferentdopants.
Protonconductivityisproportionaltoprotonmobility($\mu_{OH^\bullet}$,m^{2}V^{-1}s^{-1})andprotondiffusivity ($D_{OH^\bullet}$,m^{2}s^{-1})accordingtoequations(8)and(9),respe ctively,

$$\sigma_{OH^\bullet_O}=$$

$$\frac{z_{OH_O^\bullet}F[OH_O^\bullet]\mu_{OH_O^\bullet}}{V_M}$$

(8)

$$\sigma_{OH_O^\bullet}=\frac{z^2\bullet f^2[OH_o^\bullet]D_{OH^\bullet}}{OH_O}$$

o

(9)
$$V_M RT$$

where $z_{OH^\bullet_O}$ is the proton charge, F is the Faraday constant, V_M is the molar volume of the ceramic $(m^3 mol^{-1})$, and R is the gas constant. $D_{OH^\bullet}$ and $\mu_{OH^\bullet}$ are related through the Nernst–Einstein equation, as

o   o

shown in equation (10)
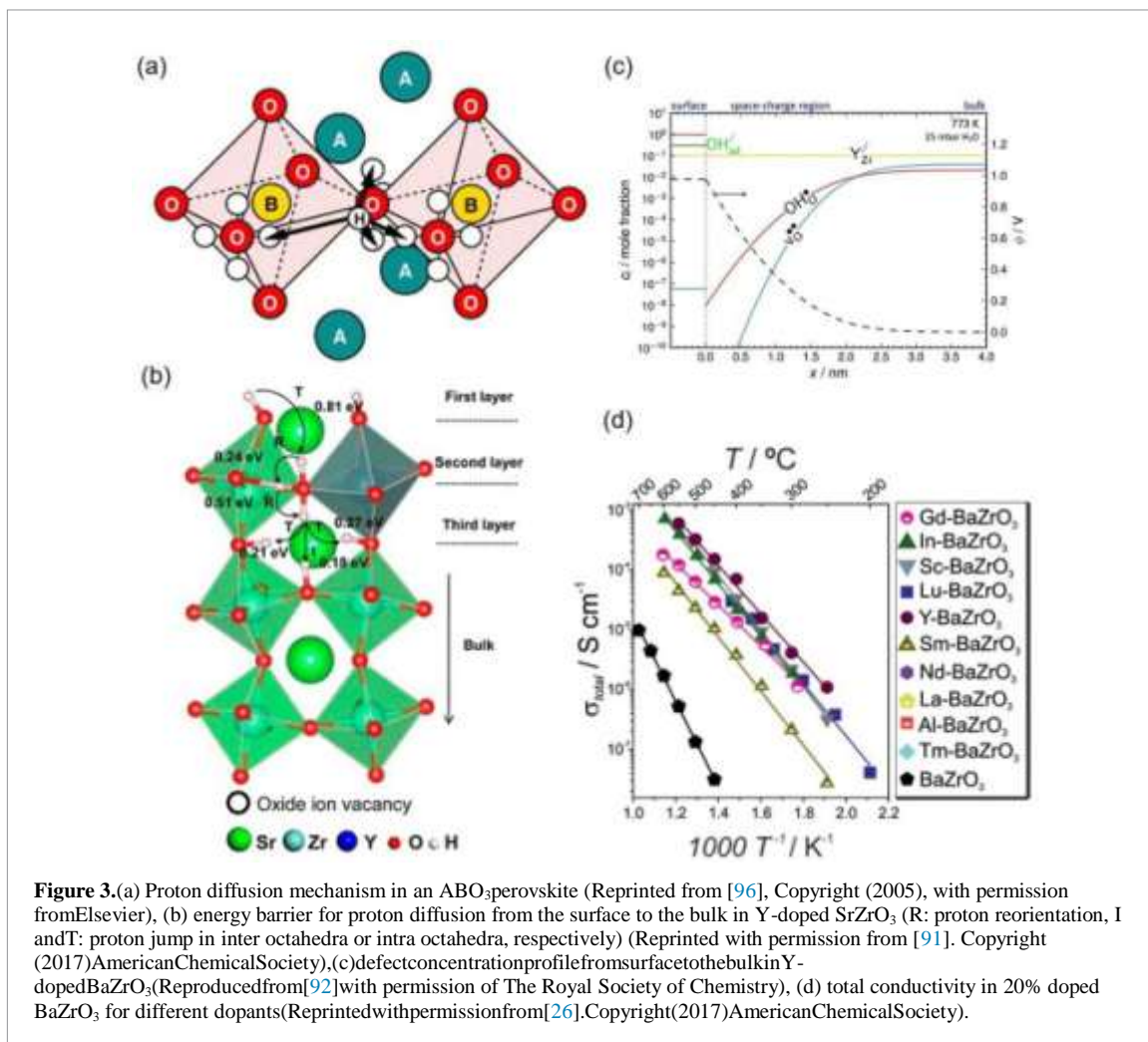
Figure 3.(a) Proton diffusion mechanism in an ABO$_3$perovskite (Reprinted from [96], Copyright (2005), with permission fromElsevier), (b) energy barrier for proton diffusion from the surface to the bulk in Y-doped SrZrO$_3$ (R: proton reorientation, I andT: proton jump in inter octahedra or intra octahedra, respectively) (Reprinted with permission from [91]. Copyright (2017)AmericanChemicalSociety),(c)defectconcentrationprofilefromsurfacetothebulkinY-dopedBaZrO$_3$(Reproducedfrom[92]with permission of The Royal Society of Chemistry), (d) total conductivity in 20% doped BaZrO$_3$ for different dopants(Reprintedwithpermissionfrom[26].Copyright(2017)AmericanChemicalSociety).

Table2. Activationenergy,E$_a$,andtotalconductivityinwetreducingorinertgas,σ$_{total}$,at600°CofvariousdopedBaZrO$_3$.

Material	E$_a$(eV)	Reference	σ$_{total}$(Scm^{-1})	Reference
BaZr$_{0.9}$Y$_{0.1}$O$_{3-\delta}$	0.43	[5]	—	
BaZr$_{0.8}$Y$_{0.2}$O$_{3-\delta}$	0.48	[5]	0.004	[93,94]
			0.0125	
BaZr$_{0.7}$Y$_{0.3}$O$_{3-\delta}$	—		0.0011	[93]
BaZr$_{0.6}$Y$_{0.4}$O$_{3-\delta}$	—		0.0007	[93]
BaZr$_{0.9}$Sc$_{0.1}$O$_{3-\delta}$	0.50	[5]	—	
BaZr$_{0.8}$Sc$_{0.2}$O$_{3-\delta}$	0.50	[51]	0.005	[51]
BaZr$_{0.9}$Gd$_{0.1}$O$_{3-\delta}$	0.47	[5]	—	
BaZr$_{0.8}$Gd$_{0.2}$O$_{3-\delta}$	—		0.0002	[26]
BaZr$_{0.9}$In$_{0.1}$O$_{3-\delta}$	0.48	[5]	—	
BaZr$_{0.8}$In$_{0.2}$O$_{3-\delta}$	—		0.0006	[95]
BaZr$_{0.5}$In$_{0.5}$O$_{3-\delta}$	0.62	[52]	—	
BaZr$_{0.25}$In$_{0.75}$O$_{3-\delta}$	0.40	[52]	—	
BaZr$_{0.8}$Sm$_{0.2}$O$_{3-\delta}$	—		0.00009	[26]

$$\frac{D_{OH_O^{\bullet}}}{\mu_{OH_O^{\bullet}}} = \frac{RT}{z_{OH_O^{\bullet}}F}$$

.(10)

Theactivation energies(seeequation (1))obtainedfrom conductivitymeasurements are frequently reportedandtable2showstheactivationenergyofvariousdopedBaZrO$_3$withallmaterialsintherangeof0.4–0.6eV.As seen in table 2, the choice of dopant and dopant concentration can modify the activation energy forproton conduction. For example, the activation energies from the same study at 10% doping are 0.43 eV forY,0.50eVforSc,0.48eVforIn,and0.47eVforGd[5].Additionally,theeffectofthedopantchoiceonprotondiffusivitycanbeappreciatedinfigure3(d)wheretheconductivitydifferencesareabouttwoordersof magnitudefordifferentdopants[26]andontable2whererepresentativeconductivitiesat600°Careshown.

Consequently,understandingtheprotonconductionphenomenaandhowdifferentmaterialsandmaterialdopingcan modify proton conductionis central to advancing proton-conducting materialsresearch. Itisworthmentioningthattheconductionofoxygenions(orV$_O^{\bullet\bullet}$)canalsoexistinproton-conducting oxides.Somestudieshaveshownoxygenionconductionatlowoxygenpartialpressuresanddryconditions [97–99] at increased temperature, usually above 700 °C [100, 101]. This mixed proton and oxygen ionconductionintheelectrolytehasbeenreportedtobebeneficialforsolidoxidecells.Forexample,studies haveshownanincreaseofefficienciesinfuelcelloperation[23,102,103]and,whensteamisaddedtobothelectrodes in electrolysis operation, an increase on the hydrogen production due to the simultaneous waterelectrolysisonbothelectrodes[19].Nevertheless,itshouldbeconsideredthatthegainofadditionaloxygenion conduction doesnotdiminishtheproton conductivitydueto theconditionsnecessaryfor theoxygenionconduction.

Protontrappinganditseffectonprotontransport
Proton trapping reduces the proton mobility and is manifested in the increase of activation energy for protonconductionatlowertemperatures[88].Atlowtemperatures,theprotonsdonothaveenoughenergytomove from the trapping positions, hence the nonlinearity of the activation energy seen for this temperaturerange. This phenomenon has been receiving increased attention as some material applications require

anoperatingtemperaturerangethatcouldfallundertheprotontrappingregime.Evidenceofprotontrappingrequires the probingof protonposition neardopant atoms.However, computational methodshave predictedprotontrappingconditions.Figure4(a)showsa schematicrepresentationofprotonbindingenergies for Y-dopedBaZrO$_3$fordifferentprotonconfigurations,wheretheprotonconfigurationinbetweentwoYatomshasthehighestbindingenergy[104].

In section 3 it was pointed out that increasing doping concentration increases proton trapping.Nonetheless, computational work has found that as proton trapping increases due to higher protonconcentrationthereisapointwherethetrappedprotonspreventotherprotonsfrombeingtrappedandpercolation channels form due to the overlap of trapping zones, and hence the proton mobility increasesagain [105, 106]. However, the doping concentration for the formation of percolation channels could bedependent on the dopant element. Additionally, proton-proton interactions could have a negative effect onproton mobilitywithincreasingprotonconcentration duetotheirrepulsive interaction[106].However,in20% Y-doped BaZrO$_3$, such negative interactions are not dominant, and instead, the trapped protonsenhancetheprotonmobilityofthefreeprotonsbyfillingthetrappingpositions[106]. Defectassociationsalsohaveaneffectonprotontrapping.Oxygenvacanciesanddopantatomscanformanassociationthatcouldpreventthe trappingeffect (figure2(b)) [53,77].Ontheotherhand,the dopant-dopantassociationcanmodifytransportpropertiesofthematerialandcouldenhanceprotontrapping[107].ADFTstudylookingatY–Ydefectassociationsandtheireffectonprotontrapping on Y-dopedBaZrO$_3$suggestedthatatriangularconfiguration ofYassociationsisresponsiblefortheprotontrapping phenomena observed in Y-doped BaZrO$_3$ [107], as shown in figure 4(b). For Y-doped BaZrO$_3$,studieshavesuggestedthattheY–Yassociationsincreasewithdopingconcentration[107,108]. Finally,dopingconcentrationanddopantelementchoiceyieldvariedeffectsonprotontrapping.

Figure 4(c) shows conductivity as a function of Y doping concentration, and it can be observed that there isan optimum concentration where conductivity is maximized [107]. However, the ideal doping level fordifferent elements may not necessarily be the same. Figure 4(d) shows proton

conductivity as a function ofproton trapping for different dopant elements for BaZrO₃, where the correlation shows that for favorableprotontrappingenergiestheprotonconductivitydecreases[85].Amidallthesetransportphenomena,theanalysisofprotonconductivityatspecificoperatingconditionsshouldbecarefullyconsideredandabalancebetweendopingconcentration,protonconcentration,andprotonmobilityisessential.

Electronicconductioninsolidoxides
In addition to the proton conduction of BaZrO₃-

based electrolytes, electronic defects such as hole defects($h^{\bullet}$) are formed by the oxidation of oxygen vacancies according to equation (11). Hole defects can beconsidereda mainchargecarrierundercertain experimentalconditions,typicallyunderhigh oxygenpartial pressuresanddryconditions[2,99,109].Therefore,theimplicationsofelectronicconductioninsolidoxidesare brieflydiscussed

$$\frac{1}{2}O_2 + V_o^{\bullet\bullet} \leftrightarrow O_o^x + 2h^{\bullet} \quad (11)$$
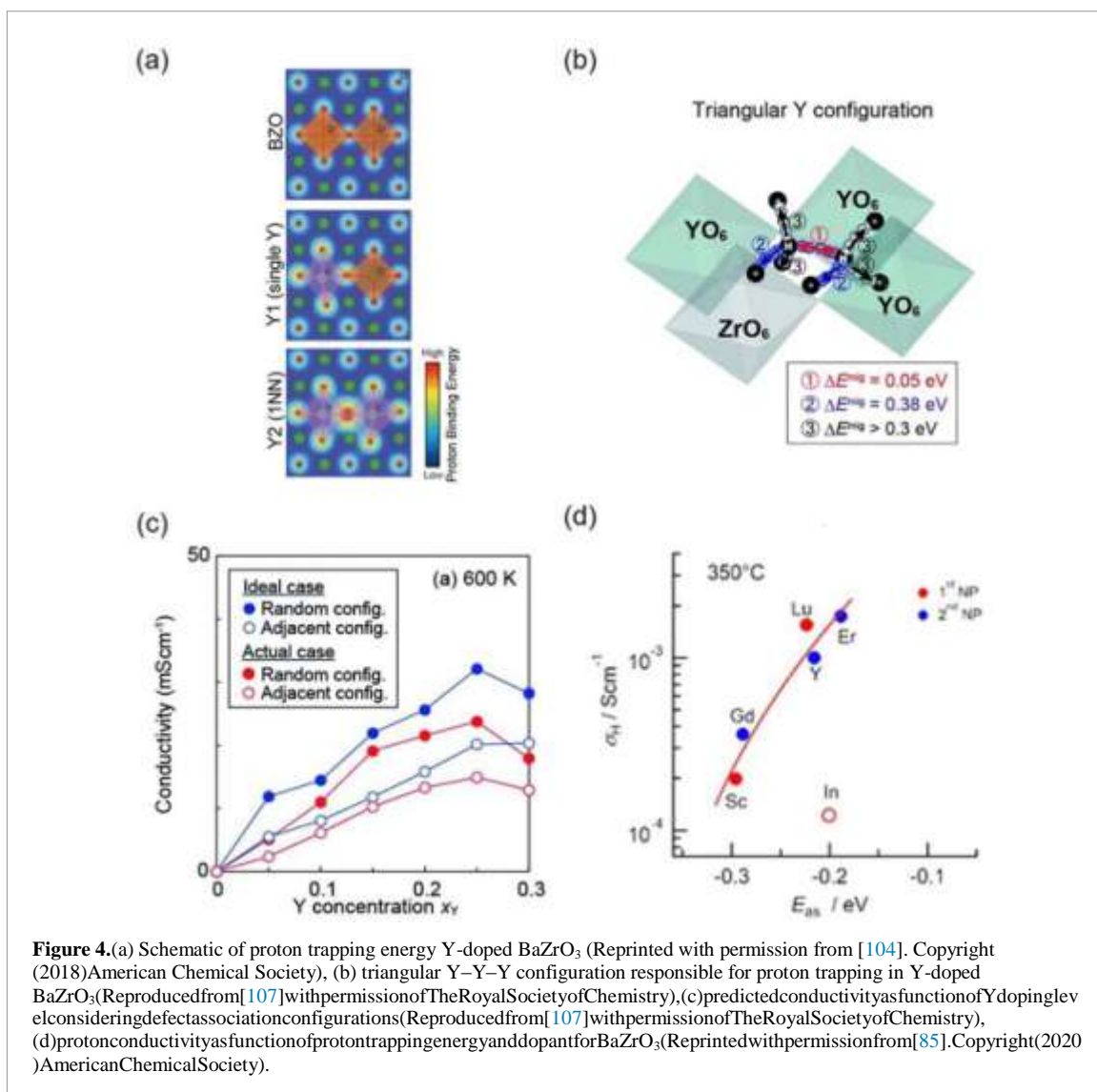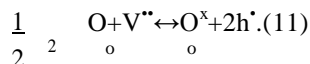

Figure 4.(a) Schematic of proton trapping energy Y-doped BaZrO₃ (Reprinted with permission from [104]. Copyright (2018)American Chemical Society), (b) triangular Y–Y–Y configuration responsible for proton trapping in Y-doped BaZrO₃(Reproducedfrom[107]withpermissionofTheRoyalSocietyofChemistry),(c)predictedconductivityasfunctionofYdopinglevelconsideringdefectassociationconfigurations(Reproducedfrom[107]withpermissionofTheRoyalSocietyofChemistry), (d)protonconductivityasfunctionofprotontrappingenergyanddopantforBaZrO₃(Reprintedwithpermissionfrom[85].Copyright(2020)AmericanChemicalSociety).

Themainconcernforelectronicconductionisrelatedtotheelectronicleakageinp-SOECs,wheresuchleakage decreases the Faradaic efficiency [10, 17, 21]. Several advances have been made towards theunderstandingofholeconduction,suchasthedevelo

pmentofdefectchemistryandtransportmodelsthathighlighttheconditionsbenefittingholeformationandconduction[17,21,110–113].
The effect of electronic defects on material hydration has also been studied. Theoretical models

havesuggested that electronic defects have the potential to modify the material hydration by the formation ofdeep acceptor states [75, 76]. Additionally, the nonlinearity of the hydration isobars has been attributed toelectronic defect formation [50]. Experimental studies have also shown a two-fold proton diffusion from thesurfacetothebulkofthematerialunderhightemperaturesandhighoxygenpartialpressuressuggestingthatthe hole conduction decouples the diffusion of protons and oxygen vacancies [114, 115]. Thus, thedominance of oxygen vacancy hydration over oxidation is critical to the understanding of material hydrationandsubsequentprotonandelectronicconductioninsolidoxides.

Concludingremarksandprospects
As discussed in this mini review, attention must be given not only to the choice of dopant but also to itsconcentration.Highdoping concentrationscanbestrategicfor improvingproton concentration, aspresentedbyarecentworkinSc-dopedBaZrO₃[51].Whiletheeffectofpercolationchannelsforprotonconduction and different defect associations can be further explored for high doping materials, someproblematic aspects of high concentration of dopants such as phase stability and sinterability should beconsidered.

A comprehensive study of the effects of the gas condition on proton conduction in these materials isnecessary.Theunderlyingmechanismresponsibleforprotonconductivitydifferencesasafunctionofthegas condition remains unclear for the most part, especially when it comes to how proton conduction is affectedby high steam concentrations and highly oxidizing atmospheres. Hence, the effect of gas conditions on thethermodynamicsandtransportphenomenashouldbethoroughlyconsidered.
Finally, coupling advanced characterization techniques with simulations could enhance theunderstandingofprotonconductionmechanisms,particularlyprotonformationanddiffusion.Byinputting proton conduction parameters, the developed models will be able to predict relevant p-SOECs propertiessuchasprotoncurrentdensityandefficiency asafunctionofoperatingconditions.

Dataavailabilitystatement
Nonewdatawerecreatedoranalysedinthisstudy.

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