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Opportunities and challenges for direct electrification of chemical processes with protonic ceramic membrane reactors

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Abstract

The necessity of developing sustainable energy storage and process electrification technologies has built an unprecedented momentum for protonic ceramic membrane reactors (PCMRs). PCMRs are practically electrolytic cells (or even fuel cells in case of cogeneration) that extend beyond the classical approach of electrolysis towards producing a variety of value-added chemicals or fuels. The use of a ceramic electrolyte membrane to electrochemically supply or remove hydrogen offers unique advantages, such as process intensification, cogeneration of chemicals and electricity, as well as the shift of the chemical equilibrium to the desired products. During the last few years, rapid progress has not only been made in the cell components, but also for upscaling, which reveals their high potential in terms of efficiency and flexibility. Herein, we discuss recent innovations and breakthroughs in the PCMR concepts and components for different processes, while we attempt to identify challenges that may hinder their wide deployment. Closer to commercialization is the production of pressurized hydrogen from sustainable sources, i.e. biogas and ammonia, while significant advancements have been made in reversible H₂O electrolysis systems. CO₂/H₂O co-electrolysis, hydrocarbon conversion and ammonia synthesis have been also successfully demonstrated, albeit with different obstacles related to the product selectivity and stability of the cell reactors. We conclude that future projects should target beyond the experimental discovery of materials, such as, multiscale modeling that would aid optimization of the involved surfaces, interfaces, and the operating parameters towards enhancing the viability of electrosynthesis in PCMRs.

1. Introduction

As a major contributor to the global greenhouse emissions, the commodity chemical industry should be modernized by being coupled with renewable electricity and neutral carbon sources to gain independence from fossil fuels. Electrification of the chemical industry through Power-to-X (X: chemicals or fuels) technologies is considered one of the promising solutions for a sustainable future by offering unique advantages for the production of valuable commodity chemicals from abundant feedstocks, such as carbon dioxide, water (and steam), dinitrogen, biomass or biogas with high efficiency at milder conditions [1–5]. These environmentally friendly but in practice impossible reactions for thermochemical reactors (e.g. for water splitting) are enabled through the direct transduction of electrical power to chemical bonds [6]. Besides the important process advantages due to direct electrification, solutions for grid-scale electricity storage and bulk transport (e.g. pipelines or sea) of renewable power as chemical energy are also enabled in such paradigms [3].

Electrochemical energy storage, as currently realized in modern fuel cells and electrolyzers, is compact, modular and quiet, which renders relative systems attractive for energy storage approaches. Electrochemical Membrane Reactors are practically electrolysis cells (or fuel cells in case of cogeneration) that extend beyond

the classical approach of water splitting and they can exhibit increased yields towards production of useful chemicals or/and electrical energy [7–9]. EMRs consist primarily of an electrolyte membrane, which allows the *in-situ* supply or removal of one of the reactants or products, respectively from/to a separate chamber in the form of an ion. This offers several advantages, such as the simultaneous production and separation of a useful product (e.g. hydrogen) in a single device, cogeneration of chemicals and electricity, as well as the shift of the chemical equilibrium to the desired products [7–11].

To this direction, EMRs which employ a solid electrolyte ceramic membrane as their main component have gained significant interest due to their structural and mechanical stability at high temperatures at which higher efficiencies can be obtained and industrially relevant reactions take place [10-13]. Solid electrolytes belong to the general category of inorganic dense membranes [11]. The ceramic electrolyte is routinely sandwiched between two solid porous electrodes, allowing the exchange of various ionic species e.g. O^{2-} , H^+ , Na⁺, Li⁺, etc. Of particular interest are the membranes that conduct O^{2-} and H^+ species since most of the reactions in chemical industry involve oxidations and (de)hydrogenation processes, providing an exciting platform for innovation in the field of electrification. Several recent and older reviews have described the use of oxide ion and proton conductors from the solid oxide electrolyzers perspective [14–19] but here we are focusing on the potential of the EMRs for chemical conversion.

The discovery of high temperature proton conductors by Iwahara *et al* [20, 21] in the early 80 s enabled the construction and development of the first high temperature solid state protonic electrochemical cells. Since then, numerous materials have been discovered [22–24] that exhibit proton (H^+) conductivity at elevated temperatures (400 °C–700 °C) having significant applications for chemical processes due to the exchange of electrochemical hydrogen in critical (de)hydrogenation reactions. The first works on chemical reactors were carried out in the 90 s and the 00 s with the first reports being on methane activation, ammonia synthesis at atmospheric pressure, hydrocarbon dehydrogenation and electrochemical promotion of catalysis [13, 25–27].

However, it was not until the last decade that the protonic membrane manufacturing took a great boost due to the development of high conductivity cells based on mixed NiO-BaZrO₃-BaCeO₃ oxides with tubular or planar geometry of low thickness [28–33]. The BaZr_{1-x-y}Ce_xY_yO_{3- δ}(BZCY) electrolyte films are typically supported on a porous Ni-BZCY support, which concurrently serves as one of the electrodes. Such cells allow significant protonic fluxes with high transport numbers, exhibit appreciable mechanical strength and chemical stability, and have thus been the main component of proton ceramic membrane reactors (PCMRs) [26, 34–38]. In the present work, we discuss important innovations and breakthroughs in electrode and electrolyte materials, as well as concepts or designs in the different catalytic processes (figure 1), namely:

- (a) Steam electrolysis for green hydrogen production
- (b) Carbon dioxide valorization to value added chemicals/fuels
- (c) Methane (or biogas) activation to olefins, aromatics and syngas
- (d) Ethane and Propane dehydrogenations
- (e) Ammonia synthesis and decomposition for green hydrogen storage

We also attempt to confront the challenges that hinder their wide deployment, while an effort is given to identify solutions for overcoming these hurdles. The last part of this work discusses opportunities, directions and possible dead ends for the PCMR technologies with the overall objective to identify key, recent, and authoritative references for the reader to delve further into.

2. The heart of the PCMR: the proton conducting electrolyte

The solid electrolyte is one of the building blocks of PCMRs along with anodic and cathodic electrocatalysts. It has a significant impact on the cell performance since it will determine the proton flux and therefore, the hydrogen supply or pumping rate during the electrochemical reactions. To this end, the candidate materials should possess high ionic conductivity with negligible electronic conductivity to avoid electron leakage. The electrolyte should also be highly dense to hinder possible gas crossover between the anodic and cathodic chambers that will have an impact on the open-circuit voltage. Chemical stability under various operation conditions, such as oxidizing and/or reducing environments, as well as steam and/or carbon-containing gas atmospheres accompanied with chemical compatibility with the neighboring electrocatalysts are of essence.

Since the pioneering works of Iwahara and co-workers, different crystal structures including perovskites, ortho-phosphates, ortho-niobates and ortho-tantalates have been proposed as protonic electrolytes [22]. Apart from BZCY-type electrolytes, different oxides have also been reported to offer promising proton conductivity <600 °C. Among them, lanthanum tungstate (LWMO) [38], F-doped LWMO





(La_{5.5}W_{0.6}Mo_{0.4}O_{11.25-δ} F_x) [39, 40], Cl-doped LWMO [41] showed satisfying hydrogen permeability and stability.

Till today, ABO₃ perovskites are the ones with the widest deployment due to their low activation energy for proton transport [24]. Proton transport requires local defects in the solid, such as oxygen vacancies in order to react with steam and produce protons through the hydration reaction:

$$H_2O_{(g)} + V_0^{"} + O_0^x \to 2OH_0^{"}$$
(1)

where V_{0}° , O_{0}° and OH_{0}° represent oxygen vacancy, lattice oxygen, and proton, respectively [42]. In addition, the Grotthuss mechanism suggests that formed protons reorient to a lattice oxygen, and then hop to the nearest oxygen ion through an OH–O bond formation. These mechanisms indicate that the local V_{\odot}° concentration and the proton mobility rate determine the proton conductivity of perovskite oxides (PO) [43]. Based on these considerations, $BaZrO_3$ theoretically displays the highest bulk proton conductivity due to its higher symmetry and unit cell volume of the crystal which are combined with high chemical and structural stability [22, 24, 32, 33, 44]. Nonetheless, different experimental findings showed that the acceptor-doped BaCeO3 displays the highest H⁺ fluxes due to lower grain boundary resistance and better sinterability, but with much lower chemical stability under H₂O and CO₂ atmospheres. Hence, by successfully mixing these two oxides (Ba(Zr,Ce))O₃, a trade-off solution between conductivity $(\sim 10 \text{ mS cm}^{-1} \text{ in humidified atmospheres})$ and the chemical/mechanical structure is stabilized by doping yttrium oxide [34, 45, 46].

Several efforts towards maximizing the proton conductivity and the sinterability of such oxides have been reported, either by optimizing the Ce/Zr ratio or attempting alternative B-site doping strategies or the addition of sintering agents (e.g. NiO or ZnO) [47]. Another interesting advancement was the doping of Yb which has been reported to increase the total conductivity and stability under carbon-rich conditions [47]. However, further experimental work is still required to draw conclusive arguments by elucidating the relationship of the structural and chemical properties of these materials with their observed performance. The above-mentioned works are clear evidence of the significant progress in the discovery and optimization of BZCY and BZCYYb materials that enabled protonic ceramic electrolytes to reach the required protonic fluxes to compete with the oxide ion SOECs.

3. Geometry considerations

Planar and tubular cell configurations are related to the development and operation of all types of solid oxide cells, including protonic ceramic reactors. The choice of cell geometry has implications on various factors, such as the conversion, product selectivity, heat dissipation and management, etc. Briefly, a planar cell exhibits a sandwich-like structure, with the dense electrolyte layer in the middle separating the anode and cathode porous layers. The dense structure of the electrolyte ensures separation of the two (porous) anode and cathode chambers and provides proton conductivity. In a proton-conducting solid oxide cell, steam is

converted to protons and oxygen (air electrode), protons transfer across the electrolyte and undergo further reactions at the other side of the cell (fuel electrode). The planar structure is the most prevalent design, since it offers the benefits of lower cost, straightforward assembly, short paths for current transport, and high output powers. However, it faces challenges regarding sealing (affecting gas-tightness) and thermal stability. Tubular configurations, on the other hand, can offer a viable alternative for sealing problems, increased scalability (stack size), improved heat distribution, but typically display lower power densities due to the higher complexity in current collection [47].

4. Reactions in PCMRs

4.1. Steam electrolysis for green hydrogen production

In PCMRs the steam electrolysis to its elements (typically called protonic ceramic electrolysis cells—PCECs when H_2O electrolysis is involved) is the most extensively studied reaction system since it offers highly efficient storage of intermittent renewable electricity as hydrogen for later use in energy applications or chemical industry. In PCEC, the steam splits at the anode (positrode) simultaneously with the oxygen evolution reaction (OER), while the molecular hydrogen is recovered at the cathodic electrode (negatrode) side:

Anode:
$$2H_2O(g) \to 4H^+ + 4e^- + O_2$$
 (2)

Cathode: $4H^+ + 4e^- \rightarrow 2H_2.$ (3)

Routinely, the protonic ceramic cells are supported on Ni-based cermets, which are also selected to serve as the cathodes of the process due to their excellent hydrogen evolution electrocatalytic properties and incapability to tolerate the highly oxidizing environments of the anode. Hence, the critical part from an electrocatalytic point of view and primary challenge of H_2O electrolysis is the choice of the anodic electrocatalyst for the OER. Based on the required properties, the suitable materials should be triple ionic-electronic conductors (TIECs, H^+/O^{2-} , e^-) with catalytic activity for OER, adequate stability under steam and oxidizing atmospheres, as well as thermal expansion coefficient (TEC) values that close to the ceramic electrolyte under reaction conditions (temperature, humidity etc). So far, numerous materials have been investigated with different types of POs and misfit-layered oxides to have shown the optimum performance [36, 47–52]. It should be pointed out that protonic ceramic electrolytes typically are not pure proton conductors and, in many cases, electronic leakage affects the performance. Therefore, when referring to the efficiency and performance evaluation of the water splitting anodes, the faradaic efficiency (FE) to hydrogen generation should be also taken into consideration besides the current density and cell voltage. The steps for water reduction on composite electrodes can be seen in figure 2 and literature data are summarized in table 1.

4.1.1. OER electrocatalysts

The BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3- δ} (BCFZY) was one of the first perovskites with high performance for H₂O splitting with FEs surpassing 90% at \geq 1.0 A cm⁻² and 600 °C under 20% H₂O. Meanwhile, BCFZY stability showed a low degradation rate (<30 mV/1000 h) after testing for up to 1200 h at 550 °C. The cell could even operate reversibly (i.e. both electrolysis and fuel cell) with considerable power-to-hydrogen efficiencies of up to 75% [48]. Besides BCFZY, the PrNi_{0.5}Co_{0.5}O_{3- δ} (PNC) perovskite displayed TIEC properties under similar conditions, particularly when a three dimensional structure was employed (figure 3(a)) [49]. The 3D PNC cell exhibited even higher current densities than BCFZY of ~1.70 and 0.80 A cm⁻² under the applied voltage of 1.4 V, at 600 °C and 500 °C, respectively, with good durability of 200 h at 500 °C in 10% steam concentration (figures 3(b) and (c)). Notably, important protonic currents were even observed at lower temperatures (0.55 A cm⁻² at 450 °C and 1.4 V). The challenge for PNC is the important thermal conductivity coefficient (TEC) mismatch with BZCY-based electrolytes and doping of Fe has been shown to improve this issue, nonetheless, in expense of performance [80].

Double perovskites are another relevant class of materials with sometimes cases of superior performance to their single counterparts. Ba_{1-x}Gd_{0.8}La_{0.2+x}Co₂O_{6- δ} (BGLC) system was extensively investigated at the University of Oslo [45]. In order to fully utilize the role of oxygen vacancy in the lanthanide layer, BGLC should sustain the active double perovskite phase. This occurs when the *x* value is ≥ 0.5 , otherwise, two-phases of BGLC and BaCO₃ may coexist [50]. Another highly active double perovskite proposed by the Haile's group is the PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+ δ} (PBSCF) (figure 3(d)), that exhibited considerable water uptake capabilities [47]. The PBSCF, however, has a mismatch in TEC with the protonic electrolyte (23.7 × 10⁻⁶ PBSCF vs 9.5 · 10⁻⁶ K⁻¹ BZCYYb). To address this challenge the same group introduced a dense PBSCF layer of ~100 nm thickness between the porous anode and the BZCYYb4411 electrolyte via



pulsed laser deposition (PLD) method, which improved the cell performance and decreased the cell resistance during electrolysis (figures 3(e) and (f)) [36].

More recently, misfit layered oxides based on $Ca_3Co_4O_{9-\delta}$ (CCO) with various dopings, such as $Gd_{0.3}Ca_{2.7}Co_4O_{9-\delta}$ (GCCO), and $Gd_{0.3}Ca_{2.7}Co_{3.82}Cu_{0.18}O_{9-\delta}$ (GCCCO) showed impressive performances, with almost the double the hydrogen production density compared to perovskites [51, 52]. Notably, this great performance was accompanied with a feeble degradation, even after 1400 h at 2.15 A cm⁻² and 600 °C testing. The same group made further progress by proposing a basic Na-doped CCO (NCCO) as an OER electrode with even higher oxygen vacancy concentration over GCCCO due to the replacement of divalent Ca^{2+} by monovalent Na⁺ (figure 3(g)). XANES and XPS techniques validated that the valence of Co ion is increased by Na doping, resulting in more unpaired electron of Co, thereby promoting the absorption of oxygen intermediates and enhancing reaction kinetics. Moreover, such oxides displayed TEC values of ~11.0 $\cdot 10^{-6}$ K⁻¹ which are close to BZCYYb electrolyte (9.5 $\cdot 10^{-6}$ K⁻¹), partially eliminating the issue of thermal expansion mismatch (figure 3(h)) [51]. It worth mentioning that the current densities are the highest to being reported in the H₂O splitting process, surpassing 6.0 A cm⁻² at 1.4 V and 600 °C (figure 3(i)), while the reversible operation could be sustained for >900 h [52].

4.2. CO₂ valorization to value-added chemicals or fuels

In the last decade, intermediate temperature $(350 \,^{\circ}\text{C}-600 \,^{\circ}\text{C})$ PCMRs have drawn significant interest for direct conversion of CO₂ into value-added chemicals by using H₂O or green H₂ as proton sources (figure 1) [54–57]. In the case steam is the hydrogen source, the reaction at the anode under external electrical potential is reaction (2) as shown above. In some cases, molecular H₂ may be the source of protons and the reaction at the anode is the reverse of reaction (3) (equation (4)). In both cases, protons are continuously transported to the cathode through the electrolyte, where they react with the CO₂ towards CO and CH₄, whereas H₂ can be formed through the side HER (equation (3)):

Anode (oxygenelectrode) : $H_2(g) + 2e^- \rightarrow 2H^+$ (molecular H_2 as reactant) (4) Cathode (Fuel electrode) : $CO_2(g) + 2H^+ + 2e^- \rightarrow CO(g) + H_2O(g) (\Delta H_{298k} = ~41 \text{ kJ mol}^{-1})$ (5)

$$CO_{2}(g) + 8H^{+} + 8e^{-} \rightarrow CH_{4}(g) + 2H_{2}O(g) (\Delta H_{298k} = \sim -165 \text{ kJ mol}^{-1})$$
(6)

$$CO_{2}(g) + 611^{-} + 6e^{-} \rightarrow CH_{4}(g) + 2H_{2}O(g) \left(\Delta H_{298k} - 6 - 105 \text{ k}\right) \text{ mor } \right)$$

$$CO_{2}(g) + 12H^{+} + 12e^{-} \rightarrow CH_{4}(g) + 4H_{2}O(g) \left(\Delta H_{298k} - 6 - 105 \text{ k}\right) \text{ mor } \right)$$

$$(0)$$

$$2CO_2(g) + 12H^+ + 12e^- \rightarrow C_2H_4(g) + 4H_2O(g) (\Delta H_{298k} = \sim -156 \text{ kJ mol}^{-1})$$
(7)

$$mCO_{2}(g) + (H^{+} + e^{-}) \rightarrow C_{2} + xH_{2}O(g) (\Delta H_{298k} < 0).$$
(8)

According to the above cathodic reactions, the electrochemical conversion of CO_2 into syngas or hydrocarbons displays high complexity. It is obvious that the formation path of two-electron-transfer product (syngas) is simpler than the generation of multi-electron-transfer products, i.e., hydrocarbons. Moreover, the challenge of the latter process increases due to the requirement of lower reaction temperatures, and cathode materials that hinder hydrogen evolution in order to increase selectivity.

To this end, the operating conditions, e.g. temperature, reactant partial pressures, reactor design, and flowrates (affecting residence time over the catalyst) are expected to have a significant impact on the product distribution [15]. Specifically, by lowering the reaction temperature, the production of methane or hydrocarbons is favored to due to the exothermicity of the reactions involved, whereas an increase in temperature favors the endothermic reverse water–gas shift and steam methane reforming reactions, resulting in the formation of CO. This imposes a challenge in case the target is the production of hydrocarbons at temperatures in which PCMR exhibit significant proton conductivity (e.g. 600 °C). Even with high conductivity at lower temperatures (<600 °C), the kinetic factors should be also taken into

				•					
a) Green hydrogen from stean									
Working electrode (WE)	Protonic Electrolyte	Counter electrode (CE)	WE feed composition	$T, \circ C$	$U_{\rm cell}, V$	j, A cm ⁻²	² FE, %	Stability, h	References
BCFZY-BCZYYb7111	BCZYYb7111	Ni-BCZYYb7111	20% H ₂ O + 80% Air	600	~1.6	1.38	98.6 (@0.4 A cm ⁻²)	1200 (550 °C)	[48]
PNC*	BZCYYb4411	Ni-BZCYYb4411	$10\%~{ m H_2O}+90\%~{ m Air}$	600	1.4	1.72	60-80 (15% H ₂ O)		[49]
				500		0.8		>200	
				450		0.55			
BGLC/BZCY72	BZCY72	Ni-BZCY72	$1.5 \text{ bar H}_2 \text{O} (80 \text{ mbar O}_2)$	600	>1.6 V	~0.28	80% - 100%	$>700 (0.0625 \mathrm{A cm^{-2}})$	[50]
PBSCF (PLD)*	BZCYYb4411	Ni-BZCYYb4411	Air $(3\% H_2 O)$	600	1.3	1.8	76	$300~(550~^{\circ}\mathrm{C}, 1.3~\mathrm{V})$	[36]
PBSCF						1.35			
GCCCO-BCZYYB7111	BCZYYb7111	Ni-BCZYYb7111	Air $(20\% H_2 O)$	600	1.3	2.15	>80%	$1400~(2.15~{ m A~cm^{-2}})$	[51]
NCCO	BZCYYb1711	Ni-BZCYYb1711	20% H ₂ O, 80% Air	600	1.4	~5.95	96.9 (@500 ° C)	900 (FC and EC operation)	[52]
									(Continued.)

Table 1. Indicative recent literature in the most studied electrochemical processes in PCMRs.

			Table 1. (Continued.)						
b) Carbon dioxide valorization									
Working electrode (WE)	Protonic Electrolyte	Counter electrode (CE)	WE feed composition	$T, ^{\circ}C$	$j, A \text{ cm}^{-2}$	S _{CH4} , %	S _{CO} , %	$X_{\rm CO2}, \%$	References
Porous Pt Ru-Co ₃ O ₄ /BZY (the ratio of Ru on Co ₃ O ₄ is 2 wt%)	BCZY27 BaZr _{0.85} Y _{0.15} O ₃ (BZY)	Pr ₂ O ₇ -CeO ₂ /LSM/BCZY27 —	Ar (9% CO ₂ , 5% H ₂) He (5% CO ₂)	700 520–720	<0.01	 <40 H ₂ /CO ₂ = <4	100% >60 reactants H ₂ /CO ₂ ratio of 1 or 4)	17.8%	[54] [55]
						$>90 H_2/CO_2 = 7$	 		
Ni/BCZYYb4411	BCZYYb4411	BCFZY-BCZYYb4411	N ₂ (4% CO ₂ , with exhaust H ₂ recycle)	450	-1000	~85	·	~85	[56]
			$N_2 (4\% CO_2)$			~ 62		~ 55	
SFM-Ni0.175	BZCYYb1411	Ni-BCZYYb7111	Pure CO_2 (10 sccm)	400 - 600	50 - 300		97.1–99.8		[57]
CeO2/Ni-BZCYYb1711(the ratio of CeO2 on cell is 3 wt%)	BZCYYb1711	PBSCF-BZCYYb1711	Ar (5% CO ₂)	550	1250	17	20		[58]
Ni-BZCYYb1711						5	23		
Ca0.4/Ni-BZCYYb4411 Ni: R7CVVh4411	BZCYYb1711		N ₂ (CO ₂)	300		87.49 2.85		57.86 31.68	[59]
Ni-BCZYYb7111 + a fixed bed	BCZYYb7111	BCFZY-BCZYYb7111	4.2% CO ₂ , 95.8% Ar	600	-2308	99.1		~80	[48]
of Ni/ CeO ₂ at 300 °C Ni-BCZYYb7111						7.1		~ 38	
BZCY72-Ni	BZCY81	BZCY72-Ni	Ar (2% CO ₂ , 4% He)	450		99 (H_2/CO_2 ratio of 4	$) \sim 0$	86	[38]
									Continued.)

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			Table 1. (Continued.)							
c) Methane activation										
Reaction	Working electrode (WE)	Protonic Electrolyte	Counter electrode (CE)	$T, \circ C$	$j, A \text{ cm}^{-2}$	$\mathrm{U}_{\mathrm{cell}}, V$	$X_{\mathrm{CH4}},$ %	Sprod., %	Stability, h	References
$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$	Ni-BZCY72	BZCY72	Cu	650	0.0113	2.4	80	~ 95	24	[45]
$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$	Ni-BZCY	$BaZr_{0.8-x-y}Ce_xY_yO_{3-\delta}$	Ni-BZCY	800	4	${\sim}0.46$	~ 100	98	2000	[60]
$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$	Ni-BZCY81	BZCY72		800	0.69	222	>99		1400	[33]
$\rm CH_4 + \rm CO_2 \rightarrow \rm 2CO + \rm 2H_2$	PBM-Ni ₄ Co-BZCYYb	BZCYYb	$NdBa_{0.75}Ca_{0.25}Co_2O_{5+\delta}$	700	4	~ 0.5	>97	222	50	[61]
$\rm CH_4 + \rm CO_2 \rightarrow \rm 2CO + \rm 2H_2$	Ni-BZCY	BZCYYb	LSCF-BZCY/R-PCeCN	700	1.45	0.5	~ 89	88	160	[62]
$6\mathrm{CH}_4, \rightarrow \mathrm{C}_6\mathrm{H}_6 + 9\mathrm{H}_2$	Cu + 6Mo/MCM-22	BZCY72	Ni-BZCY72	700	0.040	222	~11	>85	45	[34]
	catalyst layer									
$6CH_4, \rightarrow C_6H_6 + 9H_2$	${ m BaFeMo_2O_{6-\delta}}$	BCZY27	${ m BaFeMo_2O_{6-\delta}}$	750						[63]
$6CH_4, \rightarrow C_6H_6 + 9H_2$	LSCM or LSM	BCZY27 + Pt	CeO ₂	700						[64]
										(Continued.)

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d) Ethane and Propane dehydroge	nation									
Reaction	Working electrode (WE)	Protonic Electrolyte	Counter electrode (CE)	$T, \circ C U_{\alpha}$	ц, V <i>j</i> , A ст.	Power (FC), ⁻² mW cm ⁻²	Xalkane, 9	% Sprod.,%	Stability,	h References
$\begin{array}{c} C_2H_6 \to C_2H_4 + H_2 \\ C_3H_8 \to C_2H_4 + H_2/C_3H_6 + H_2 \end{array}$	$\begin{array}{l} Co-Fe-(Pr_{0,4}Sr_{0,6})_3(Fe_{0.85}Mo_{0.15})_2O_7\\ (Pr_{0,3}Sr_{0,7})_{0,9}Ni_{0,1}Ti_{0,9}O_3/Ni-BZCY\end{array}$	$\begin{array}{l} BaCe_{0,7}Zr_{0,1}Y_{0,2}O_{3-\delta}\\ BZCY \end{array}$	LSCoF LSCF/BZCY	750 1.0 750 ~ 0	05 0.66 .7 0.300	348.8 450	~50 72	>91 31 C ₂ 35 C ₃	100 50	[65] [66]
$\rm C_2H_6 \rightarrow C_2H_4 + H_2$	$(PrBa)_{0.95}(Fe_{0.9}Mo_{0.1})_2O_{5+\delta}/Ni-BZCY$	BZCY	$(PrBa)_{0.95}(Fe_{0.9}Mo_{0.1})_2O_{5+\delta}$	550	0.040		~ 40	(0- 0co) 66.7	28	[67]
										(Continued.)

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e) Ammonia synthesis and deco	mposition							
Reaction	Working electrode (WE)	Protonic Electrolyte	Counter electrode (CE)	$T, ^{\circ}C$	$\mathbf{U}_{\text{cell}},\mathbf{V}$	$j, A \text{ cm}^{-2}$	Rate of production	References
$ m N_2 + 3H_2 ightarrow 2 m NH_3$	Pd	$SrCe_{0.95}Yb_{0.05}O3$ (SCY)	Pd	570		< 0.002	$10^{-8} \text{ mol} \cdot \text{s}^{-1}$	[68]
$ m N_2 + 3H_2 ightarrow 2NH_3$	Ni–BaZr _{0.7} Ce _{0.2} Y _{0.1} O _{2.9}	BZCY72	porous Cu	620	2.4	~ 0.026	$4.1 \cdot 10^{-8} \text{ mol s}^{-1} \text{ cm}^{-2}$	[69]
$N_2 + 3H_2 \rightarrow 2NH_3$	NiO-CeO ₂	BCZYZ	$\overline{F}e_2O_3$	450	1.05		$4 \cdot 10^{-9} \text{ mol} \cdot \text{s}^{-1} \text{ cm}^{-2}$	[20]
$N_2 + 3H_2 \rightarrow 2NH_3$	Fe-K-NiO-BCZG	$BaCe_{0.7}Zr_{0.1}Gd_{0.2}O_{3-\delta}/Li_2CO_3$	NiO-BCZG	500	0.8	0.01	$1.87 \cdot 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$	[71]
$CH_4, H_2O \rightarrow NH_3, CO_2, H_2$	VN-Fe	$BaZr_{0.8}Ce_{0.1}Y_{0.1}O_{3-\delta}(BZCY81)$	Ni-BaZr _{0.7} Ce _{0.2} Y _{0.1} O _{3-δ}	600	0.63	222	$68 \text{ mmol } h^{-1} \text{ m}^{-2}$	[72]
$N_2 + 3H_2 \rightarrow 2NH_3$	Ni-BCZY	$\mathrm{BaCe}_{0.2}\mathrm{Zr}_{0.7}\mathrm{Y}_{0.1}\mathrm{O}_{3-\delta}$	Pt	500	2.75	0.080	$26.8 \text{ nmol s}^{-1} \text{ cm}^{-2}$	[73]
$2\mathrm{NH}_3 ightarrow \mathrm{N}_2 + 3\mathrm{H}_2$	Ru-LWO	La _{5.5} WO _{11.25-δ}	Pt-LWO	350	1.2	2.5	$231.1 \ \mu { m g} { m h}^{-1} { m cm}^{-2}$	[74]
$2\mathrm{NH}_3 ightarrow \mathrm{N}_2 + 3\mathrm{H}_2$	NiO-BZCY81	BaZr _{0.8} Ce _{0.1} Y _{0.1} O _{3-δ} / BZCY81	I	650		~ 0.7		[33]
$2\mathrm{NH}_3 ightarrow \mathrm{N}_2 + 3\mathrm{H}_2$	Ni/BZCY82	BZCY82	$BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$ (BCFZY0.1)	600	I	6.0		[35]
$2\mathrm{NH}_3 \rightleftharpoons \mathrm{N}_2 + 3\mathrm{H}_2$	NiO- BaCe _{0.7} Zr _{0.1} Y _{0.1} Yb _{0.1} O	BCZYYbN		650	1.04		$1.2 \cdot 10^{-8} \text{ mol s}^{-1} \text{ cm}^{-2}$	[75]
	$3-\delta$		B.C. E. Z. V. O	2EO	20	л с Г		
$2NH_3 \rightarrow N_2 + 3H_2$ $2NH_3 \rightarrow N_3 + 3H_3$	Fe-CeO./Ni-BzCYYh	Fu-bzuiu Bzcyyh	Datton,4.50,4.510,110,103-6 PrBaneSrneCoreFeneOf	0C0	0.0 ∼0.4	C7.1		[77]
$N_2 + 3H_2 \rightarrow 2NH_3$	Sr _x Ti _{0.6} Fe _{0.4} O _{3-δ} (x = 1, 0.9)	BZCYYb	NiO/BZCYYb	650	0.6	0.0012	$6.84 \cdot 10^{-9} \text{ mol } \text{s}^{-1} \text{ cm}^{-2}$ (x = 1) (x = 1, -2, -1, -2, -2, -2, -2, -2, -2, -2, -2, -2, -2	[28]
$ m N_2+3H_2 ightarrow2 m NH_3$	LaCu _{0.1} Fe _{0.9} O ₃₋₆ /BZCYYb	BZCYYb	Ni/BZCYYb	650	0.4		(x = 0.9) $(x = 0.9)$ $(x = 0.9)$	[62]

Table 1. (Continued.)



PNC perovskite, (b) SEM image of 3D structured PNC, (c) Impedance spectra revealing the enhancement due to 3D-structure of the stability. (a)–(c) Reproduced from [49]. CC BY 4.0. (d) Crystal structure of PBSCF double perovskite (e) SEM cross section image of the PLD PBSCF cell and (f) PBSCF with extra PLD layer benchmarking vs bare PBSCF, and standard air perovskite electrodes. (e) Reproduced from [47], with permission from Springer Nature. (f) Reproduced from [36] with permission from the Royal Society of Chemistry. (g) Crystal structure, (h) TEC and (i) IV polarization curves of NCCO. (g)–(i) [52] John Wiley & Sons. © 2022 Wiley-VCH GmbH.

account; HER dominates on metal surfaces, while on typical cathode-supported cells of Ni-BZCY, the reduction of CO_2 to CO is faster. Nevertheless, when the H_2/CO_2 ratio increases due to the higher current densities and thus, proton fluxes, the hydrocarbon formation is favored as shown by the stoichiometry of reactions (6)–(8).

It is therefore apparent that the selection of the cathodic electrocatalyst plays a decisive role in CO₂ conversion process. Extensive research has been devoted to developing new or modifying existing cathodic materials [54–59, 81–84]. For instance, by engineering the surface of CeO₂, Ye *et al* significantly enhanced CO₂ methanation [58], reaching CH₄ selectivity in the cell of 17%, but at production rate of only 0.19 ml min cm⁻² at 550 °C. These values were further improved by Pan *et al* [56] where a higher CO₂ conversion and a CH₄ yield of 34.6% from CO₂ and H₂O as reactants were achieved at a current density of $-1 \text{ A} \cdot \text{cm}^{-2}$ at 450 °C. The H₂-co-feed enhances CH₄ yield to 71.2% by utilizing H₂ that can be recycled in the reactor stream. The latter enhancement in the presence of gaseous hydrogen in the cathode atmospherew as partially attributed to electrochemical promotion of catalysis effect. Lastly, under fuel cell conditions (CH₄ fuel), a power density of 0.22 W cm⁻² was reached at 550 °C.

Choi *et al* proved that surface V_0^{\cdot} concentration of the catalysts was increased by tuning their surface basicity, which significantly decreases the CO₂ adsorption energy and promotes methanation [59]. The authors successfully synthesized a strong basic binary cathode of CaO-modified Ni-BZCYYb. Experimental evidence and DFT calculations (figures 4(a) and (b) suggested that CaO acts as an electron donor for the Ni-BZCYYb surface, thereby creating V_0° on the BZCYYb surface through the reduction of Ce



Figure 4. Indicative innovative concepts for CO₂ reduction. (a) CO₂ hydrogenation on the CeO₂-modified Ni-BZCYYb cathode surface. (b) Calculation of potential energy illustration for CO hydrogenation to CH₄ on BZCYYb and CeO₂. (c) Comparison of produced CH₄ with the pristine and CeO₂-modified cathode under different electrolysis currents. (a)–(c) Reproduced from [58] with permission from the Royal Society of Chemistry. (d) Schematic illustration of CO₂ reduction to CO in SFM-Ni_{0.175} cathode-based cell. CO₂ reduction paths on the (e) SFM-Ni_{0.175} and (f) Ni-BZCYYb. (d)–(f) Reprinted from [57], Copyright (2022), with permission from Elsevier. (g) High pressure CO₂ methanation in a tubular PCMR. (h) CO₂ conversion rate and i. CH₄ selectivity as a function of pressure and H₂/CO₂ ratio at 450 °C. (g)–(i) Reprinted from [38], Copyright (2023), with permission from Elsevier.

 $(2Ce_{Ce}^{\times} + O_{O}^{\times} \rightarrow 2Ce_{Ce}' + V_{O}^{\cdot})$, which in turn decreases the activation energy for CO₂ adsorption. As a result, the CaO modification doubled the conversion compared to the bare Ni-BZCYYb (figure 4(c)).

An alternative for maximizing yield to methane was proposed by Duan *et al*, by connecting the exhaust of the PCMR with an external fixed bed reactor that enabled almost complete conversion of CO_2 to methane, 14-times higher than that of the single PCECs [48]. The same group also employed the *in-situ* exsolution NiFe nanoparticles from a SrFeMo-based double perovskite cathode. The bimetallic NiFe exsolution enabled higher CO_2 conversion to CO. The authors elucidated the difference between SFM-Ni and BZCYYb-Ni for selective CO_2 conversion by *in-situ* DRIFTS. The absorbed CO_2 on SFM-Ni_{0.175} forms bicarbonate and monodentate carbonate, which were then reduced to CO, while on BZCYYb-Ni CO_2 was reduced to CH₄ and CO through formate path and the dissociative path of the monodentate carbonate, respectively [57]. An important development for CO_2 PCMRs was the recent report from Quina *et al* [38] in which a pressurized CO_2 reduction PCMR was demonstrated. The reaction was studied as a function of total pressure, temperature and H₂/CO₂ ratio resulting from the corresponding current density, reaching CH₄ yields of 99% with pressures above 20 bar. High pressure and a CO_2 -rich atmosphere ameliorated the electrochemical behavior because of higher electrolyte hydration and boosted electrode kinetics [38].

4.3. Methane and biogas activation processes

As the main constituent of natural gas, methane (CH₄) is considered an ample and versatile energy source, both in terms of its use as a fuel (e.g. shipping) and commodity chemical transformations. Thus, methane can undergo transformations in a PCMR to yield syngas, aromatics and olefins. Steam reforming of methane (SRM) is today the dominant route for the production of syngas. In 2016, Kyriakou *et al* [45] demonstrated low temperature (450 °C–650 °C) SRM by employing a Ni-BZCY72/BZCY72/Cu PCMR. The protons removal allowed the methane conversion to surpass 80% at 600 °C, which cannot be achieved in a conventional catalytic reactor operating at the same conditions of pressure and temperature. Moreover, the continuous hydrogen recovery and the decrease in operation temperature favored the water gas-shift reaction, and therefore, the selectivity towards CO₂ (~99%). Malerød–Fjeld *et al* [60] carried out SRM by using the same tubular reactor, albeit in a Ni-BZCY symmetrical configuration. Full methane conversion was achieved at 800 °C by continuously removing hydrogen, reaching impressive current densities of 4 A cm⁻². More recently, Clark *et al* [33] expanded this concept of hydrogen extraction to processes beyond SRM, such as biogas and ammonia whilst, developing a pioneering PCMR stacked module. The stack formulation enables up to 400 A of total current, H₂ production of up to 0.34 kg d⁻¹ from methane, 0.31 kg d⁻¹ from biogas, and 0.34 kg d⁻¹ from ammonia.

Dry reforming of biogas (CH₄, CO₂) is another intriguing route for generating syngas, aiming to enhance and consolidate global decarbonization protocols. Hua *et al* [61] reported on an electrochemical reactor with a Ni₄Co bimetallic catalyst on PrBaMn₂O_{5+ δ} (PBM)-BZCYYb composite anode. Notably, the authors showed electrochemical stability in a 50 ppm H₂S-containing CH₄/CO₂ mixture at a current density of 1 A·cm² with up to 0.8 W cm⁻². Wang *et al* [62] employed anode-supported cells and reported *R*_p of ~0.15 Ω and *R*_{Ω} of ~0.17 Ω at 700 °C, whereas the peak power densities reached 0.697 (with reforming layer) and 0.662 W cm⁻² (without layer), indicating that the presence of the reforming layer does not contribute significantly to the performance improvement despite its catalytic properties.

One of the first examples of methane conversion to hydrocarbons was the simultaneous production of C_2 hydrocarbons and H_2 or electricity in a PCMR (upper case of figure 1(b)) [85]. By employing an Ag cathode and LSCoF at temperatures between 700 °C–850 °C and atmospheric pressure, low power densities of <1.2 mW cm⁻² were achieved due to the ohmic resistance of the high thickness (2 mm) SrZr_{0.9}Y_{0.1}O₃ electrolyte supported cell. Interestingly, the continuous hydrogen pumping from methane in fuel cell mode resulted in an up-to 20% increase in C_2 's reaction rate compared to the open circuit operation. The overall cell reactions for ethylene as primary product are described by the following equations:

Electrolysis mode :
$$2CH_4 \rightarrow 2H_2 + C_2H_4$$
 (9)

Fuel cell mode :
$$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O.$$
 (10)

In 2016, Morejudo *et al* [34] reported on the direct conversion of methane to benzene (C_6H_6) using a BaZrO₃-based hybrid catalytic-electrochemical membrane reactor of tubular configuration that pumps hydrogen and supplies small amounts of oxygen (co-ionic) to avoid coking, leading to increased catalyst stability (figure 5). Up to 80% carbon efficiencies were reached, aiding to the process viability. Nonoxidative dehydrogenation of ethane (NDE) to wards ethylene in the presence of nitrous oxide has been realized in a PCMR bearing a supported BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3- δ} membrane, where the cogeneration of electricity and ethylene was achieved by using a PSFNCu (Pr_{0.6}Sr_{0.4}Fe_{0.8}Nb_{0.1}Cu_{0.1}O_{3- δ}) PO catalytic layer in the anode [86]:

$$C_2H_6 + N_2O \rightarrow C_2H_4 + N_2 + H_2O$$
 (11)

High performance in NDE was attributed to the stability of the perovskite during reduction and oxygen vacancies. The maximum power density was 200 mW cm⁻² (750 °C), while an ethane conversion of \sim 45% and selectivity for ethylene of \sim 93% were obtained. Incorporation of nitrous oxide conversion resulted in a 208 mW cm⁻² (750 °C) power density, 45.2% ethane conversion, 92.5% ethylene selectivity, and 19% conversion for N2O, successfully demonstrating the simultaneous conversion of greenhouse gas N2O and olefin production. A different cell reactor with a double $Ba_2FeMoO_{6-\delta}$ (BFMO) perovskite [63] was also reported for the promotion of methane dehydroaromatization (MDA) reaction in a symmetrical cell configuration. BFMO exhibited adequate compatibility with BCZY27 stability for a prolonged period under reducing conditions (5% H_2) and stability in 10% CH₄ at 750 °C. The optimized ASR of the electrode reached 6.8 Ω cm⁻² at 750 °C in a humid H₂ atmosphere. More recently, Almar *et al* [64] investigated various perovskite electrode formulations, coupled with BCZY27 electrolyte where the infiltration of Pt/CeO₂ decreased R_p to 0.7 Ω cm⁻² at 700 °C in a reducing CH₄ atmosphere. MDA at 700 °C has also been investigated using a U-shaped ceramic hollow La5.5W0.6Mo0.4O11.25-6 (LWM0.4) fiber membrane reactor with a zeolite-based catalyst (Mo/HZSM-5) [87]. Removal of H_2 was employed to overcome thermodynamic limitations to increase methane conversion and aromatics yield with the latter reaching 70%. Coking was observed due to the removal of hydrogen but regeneration afforded the recovered catalyst.

4.4. Ethane and propane dehydrogenation

Ethylene and propylene are amongst the most important compounds in chemical industry due to their use as building blocks, particularly for polymers. The combination of the PCMRs with ethane or propane dehydrogenation towards lower olefins has significant advantages. In electrolytic operation, the hydrogen is



directly separated from the dehydrogenation chamber (anode), by simultaneously shifting the equilibrium to the desired olefins and hydrogen products. Moreover, by introducing air at the cathode, the overall cell reaction becomes a partial oxidation which is spontaneous, thus offering the chance for the cogeneration of ethylene and power.

One of the first efforts to exemplify this concept was the work of Liu *et al* [65] by employing a double-layer PO $(Pr_{0,4}Sr_{0.6})_3(Fe_{0.85}Mo_{0.15})_2O_7$ (PSFM) with bimetallic exsolution of Co–Fe nanoparticles deposited over a BZCY electrolyte. The authors reported high power densities of ~0.45 W cm⁻² in ethane at 750 °C, with ethylene selectivity >91% and cogeneration of electricity. By elevating the temperature, the ethylene yield was improved but with lower selectivity due to coking. In 2020, Shi *et al* [66] reported on the generation of ethylene and propylene in using propane as feedstock. $(Pr_{0.3}Sr_{0.7})_{0.9}Ni_{0.1}Ti_{0.9}O_3$ was employed as a catalytic anode-supported layer with exsolved Ni-nanoparticles. BZCY was employed as an electrolyte, with an LSCF-BZCY cathode. In a 9:1 propane—water mixture tolerance against coking was observed, suggested to occur due to the increased activity of the catalytic layer. At 700 °C, the conversion to propylene reached 36% and to ethylene 32%, at a current density of 300 mA cm⁻². Similarly, several groups have demonstrated cogeneration of ethylene and hydrogen at elevated temperatures by changing the anodic perovskites and protonic ceramic electrolytes, achieving yields of up to 40%, but with rather low power densities for upscaling.

On the other hand, Wu *et al* [67] proposed a planar PCMR which operates at considerably lower temperatures to achieve ethane dehydrogenation (~550 °C). Alkane dehydrogenation is even more challenging at lower temperatures and therefore, the electrochemical cell reactor consisted of a highly active PtGa-ZSM-5 catalyst over a porous (PrBa)_{0.95}(Fe_{0.9}Mo_{0.1})₂O_{5+ δ} anode in a Ni-BZCYYb-based cell. The authors reported an <40% ethane conversion with an ethylene yield of up to 26.7%, however, at low current densities (40 mA cm⁻²) due to the low temperatures employed.

4.5. Ammonia synthesis and decomposition

4.5.1. Dinitrogen fixation

Ammonia synthesis from its constituent elements was always considered a holy grail for modern chemistry and engineering due to the ability of ammonia to act as hydrogen energy carrier or be further utilized in fertilizer synthesis [88]. Ammonia synthesis at atmospheric pressure in PCMRs was first reported by Marnellos and Stoukides [68] in 1998 where an Pd on SrCeYb was used to exemplify the concept while several works that followed have verified its feasibility but with poor faradaic efficiencies. More recently, Vasileiou *et al* [89] made an effort to enhance the open-circuit (catalytic) rate of a catalytically active



Figure 6. Integration of hydrogen production, purification, and ammonia synthesis in the PCMR. (A) At the Ni-BZCY72 anode compartment, (conversion of CH_4 - H_2O mixture to CO_2 and H^+ , the latter transported to the VN–Fe cathode. On VN, lattice N reacts with H^+ to form NH₃, while the N-vacancy is replenished by dissociated N₂ from the gas-phase. (B) SEM images of VN–Fe cathode surface, cell cross-section, and Ni-BZCY72 anode surface after exposure to 20% H_2/N_2 at 650 °C for 48 h. Reprinted from [72], Copyright (2020), with permission from Elsevier.

Ni-BCZY (Electrochemical Promotion of Catalysis, EPOC, study). The net electrocatalytic rate (difference between closed- and open circuit rate) was found ~ 1.5 g h⁻¹ m⁻², with faradaic efficiencies surpassing 6%. The same group used the same cell but in a double chamber configuration in order to control the co-fed hydrogen [69]. Without gaseous H₂ addition, at 620 °C the highest ammonia production rate was ~ 0.5 g h⁻¹ m⁻². However, by co-feeding N₂ and H₂ a net electrocatalytic rate of 2.4 g h⁻¹ m⁻² was reported, translating to a >140% enhancement compared to the OCV (catalytic) rate.

Klinsrisuk and Irvine [70] examined the same reaction with a different electrolyte membrane, namely BaCe_{0.5}Zr_{0.3}Y_{0.16}Zn_{0.04}O_{3- δ} (BCZYZ). The anode was NiO/CeO₂ and the cathode was a PdO-impregnated iron oxide while no hydrogen was co-fed. The electrocatalytic ammonia production rates reached \sim 3 g h⁻¹ m⁻² at 450 °C, but again with very low FEs (<2.5%). Through a different doping strategy, Lei *et al* [71] used a BaCe_{0.7}Zr_{0.1}Gd_{0.2}O_{3- δ} (BCZG) electrolyte with Li doping which enhanced ionic conductivity and acted as a co-sintering aid. Ammonia synthesis was then realized in a cell with Fe- and K-doped Ni-BCZG and Ni-BCZG electrodes. At 500 °C, a formation rate of ~0.1 g h⁻¹ m⁻² was achieved, with a current efficiency of 0.53% at 0.8 V.

With the brisk developments in tubular protonic electrolytes, Kyriakou *et al* [72] utilized a tubular barium zirconate PCMR to demonstrate the integration of all key steps of an ammonia plant, i.e. hydrogen production/purification from methane steam reforming and water gas shift, as well as ammonia synthesis, in a single PCMR (figure 6). By introducing for the first time the nitride electrodes high temperature electrochemical cells (VN–Fe) an up to 14% FE was achieved at low applied voltages for dinitrogen reduction (<0.8 V) due to the use of the Mars-van Krevelen mechanism. Practically, lattice nitrogen from the nitride reacts with protons and the vacancy in the nitride is replenished by the dissociation of the gas phase dinitrogen. The system also made use of the capability of the PCMR to shift the equilibrium of hydrogen production through its *in-situ* extraction from the Ni-BZCY anode, thus delivering almost pure CO₂ for easier capture and further use.



Another intriguing strategy to enhance the FE to ammonia in a similar PCMR was shown by Sharma *et al* [73], where protons from water oxidation reacts with the plasma-activated nitrogen molecules to yield ammonia. Ammonia production rate reached 16.4 g h⁻¹ m⁻² accompanied with an up to 88% FE at 500 °C. In order to decrease the temperature and slow down ammonia decomposition kinetics, a PCMR with a La_{5.5}WO_{11.25- δ} (LWO) membrane, a Pt@LWO anode and Ru@LWO cathode, operating at 350 °C, was fabricated by Weng *et al* [74]. A high FE of 43.8% was reported, with ammonia production rate of 2.3 g h⁻¹ m⁻² at a current density of 2.5 mA cm⁻². This reactor also displayed durability after 100 h under N₂ reducing conditions.

4.5.2. Hydrogen recovery from ammonia

The Ni-BZCY (or Yb) electrodes have shown excellent capability in decomposing ammonia to its elements, thus rendering anode-supported proton conducting cells suitable for ammonia fuel cell operation [33]. Nevertheless, besides the demonstration by Duan *et al* [35] and the work of Clark *et al* [33] discussed above, most of the research reported on anode functionalization with different active metals to achieve even higher performances. A reversible PCFC was reported by Zhu *et al* [75], comprising of a Ru-(BaO)₂(CaO)(Al₂O₃) ammonia catalyst. A maximum power output of 944 mW cm⁻² was achieved at 650 °C using NH₃ fuel (877 mW cm⁻² for H₂ fuel at the same temperature). At 600 °C, stability was displayed for 1250 h. He *et al* [76] reported a Pd-doped BZCYYb PO, namely Ba(Zr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1})_{0.95}Pd_{0.05}O_{3-\delta} that functions as electrolyte and anode. Exsolution of Pd was observed, and a superior proton conductivity compared to BZCYYb. The Ni-PdBZCYYb composite anode reached a power density of ~0.75 W cm⁻² at 650 °C with ammonia fuel. Importantly, the exsolved Pd metal sites were reported to protect Ni-particles against ammonia attack. Stability was exhibited for 350 h in H₂ and NH₃ atmospheres at 550 °C (figure 7). Hou *et al* [77], added an iron-doped ceria catalyst layer on Ni-BZCYYb anode cermet achieving 1.06 W cm⁻² at 700 °C due to the Fe-Ce catalyst inhibiting iron nitride formation (iron poisoning).

4.6. Opportunities, directions and possible dead ends

Electrification of industrial processes towards high-value chemicals or fuels by utilizing renewable sources is critical if carbon neutrality is to be achieved in the coming years. Concurrently, the direct use of hydrogen as a feedstock or product is of crucial importance for the chemical industry and in extend for our society since it diminishes the CO_2 emissions and hence, its production technology is going to have a considerable impact on energy economy. To this direction, PCMRs may be utilized not only as electrochemical reactors but also as *in-situ* separators, thus offering high energy efficiencies and flexibility to several processes of industrial interest. This is due to the integrated approach of a solid ionic membrane with a catalytic reactor that also display unique features; (a) process intensification and thus, higher efficiency through the channeling of the heat released by an exothermic reaction at one of the electrodes or the ion transport (joule effect) through the electrolyte to an endothermic reaction at the counter side (e.g. ammonia synthesis and steam methane reforming or steam electrolysis). (b) Shift of the equilibrium of the reaction for maximizing the product yield while purifying or storing hydrogen. The different processes described in the previous section of the present article clearly exemplify the applicability and the potential of the PCMR systems in processes varying from energy to environmental remediation. Below, we explore some possible directions and challenges for different processes, as well as new opportunities on unidentified or immature systems.

4.6.1. Near-term targets: SoA PCMR components and upscaling for H₂ generation

An impressive aspect is the considerable progress that has taken place in the last decade in design and fabrication of cells of both tubular and planar configurations. The two designs have their origins from the traditional oxide ion-based cells. Planar design has the advantage of lower cell reactor sizes and better current collection whereas, the tubular geometry transcends in terms of thermomechanical properties (e.g. during pressurization for H₂ recovery) and heat transfer distribution [90]. In addition to this, the choice of the geometry in PCMR can be even more significant due to the wider range of products and the sensitive balance between them in order to obtain the highest selectivity (or FE) to the desired product. The leading role in manufacturing tubular ceramic proton conducting cells has CoorsTek Membrane Sciences AS that develops a high Zr content membrane with an electrolyte thickness of 25–30 μ m. The BZCY electrolyte film is supported on a porous Ni-BZCY cermet, which, at the same time, serves as an electrode [28]. The cell allows high H⁺ fluxes (on the order of μ mol H₂ s⁻¹ cm⁻²), exhibits appreciable mechanical and chemical stability and has thus been successfully used in several cases of H₂O splitting, CO₂ valorization and hydrogen recovery at low temperatures and high pressure [33]. These cells have significantly contributed in advancing the PCMR technology as essentially meet the requirements for H^+ flux and stability to a certain extent. On the other hand, planar cells have been mainly demonstrated for PCMR applications only as button cells of a few cm² size, whilst the scaling has been carried out in some decades of cm² only in fuel cell operation. Thus, further experimental validation is necessary for evaluating their performance during water electrolysis and subsequently, as PCMRs for more complex reaction schemes [27, 91, 92].

The above-described progress in membrane materials and design in combination with an urge in the development of Power-2-X technologies for electrical power storage imply a momentum for larger scale demonstration projects to explore the potential of protonic cells. For instance, the extensively investigated reversible H_2/H_2O SOECs could lead the way for demonstration of the same concept in PCMRs but issues related to decreased FE due to electronic leakage should be addressed prior to this. Outstanding current densities have been achieved with several anodic electrodes such as PBSCF and more recently NCCO (\sim 5–6 A cm⁻² at 600 °C and around 2–3 A cm⁻² at 500 °C) that exceed commercialization targets, albeit their long-term stability is debatable. An interesting approach to be considered here is the operation of the cell in reversible mode (practically creating a hydrogen flow battery) to enhance their flexibility and possibly lifetime. The latter has been exemplified in oxide ion cells where the partial operation in fuel cell mode instead of continuous electrolysis revealed 'healing' properties [14].

Unquestionably, one of the most promising approaches for PCMR upscaling is the recovery of pressurized hydrogen from biogas, methane or ammonia feedstocks, as proposed by Clark *et al* in a tubular geometry configuration (figure 8) [33]. The authors presented a unique stack with 36 cells (584 cm², 400 A in total) of total active area with a novel interconnect material that achieves complete conversion of the feedstocks as well as >99% recovery to pressurized hydrogen of up to 140 bar when ammonia was employed. This PCMR approach is benefited by the high hydrogen concentrations produced even when no current or voltage is imposed (open-circuit conditions). For instance, ammonia decomposition takes place spontaneously at high temperatures over an effective catalyst (as Ni-BZCY) which in turn benefits the FE since hydrogen oxidation to protons is much simpler compared to OER (i.e. H₂O splitting). Additionally, proton pumping shifts the equilibrium to the desired hydrogen production side during the separation (process intensification), while high efficiency can be achieved due to channeling of heat to the endothermic anodic reactions through the joule effect. The system reported by CoorsTek currently generates ~0.5 kg d⁻¹ of hydrogen and it could be the bellwether system for navigating the developments of upscaling projects, hence validating the potential for commercial viability of the PCMR's in the coming years.

4.6.2. Long-term targets: chemicals and fuels beyond hydrogen

The production of hydrocarbons from the conversion of carbon dioxide or alkanes displays another attractive direction towards chemical energy storage as evident from the extensive number of reported works on electrocatalytic and membrane materials, as well as alternative concepts. Co-electrolysis of CO_2 and H_2O is an aspect shown by Irvine's group more than a decade ago, followed by the ground-breaking developments in membranes and positrodes by O'Hayre's and Haile's groups. The main product under the operating conditions was syngas while methane was produced at minor concentrations below 500 °C due to thermodynamic and kinetic limitations, i.e. low H/C ratios due to the decreased proton flux. This challenge was addressed by O'Hayre's group through the downstream catalytic methanation of the produced syngas at 300 °C in order to achieve higher methane yields [35].

The single-step approach can be rather beneficial and it came through the development of high performance and pressurizable proton conducting membranes that enabled appreciable proton flux below 500 °C by simultaneously creating favorable thermodynamics for direct methanation. It should be noted, however, that complete conversion of CO_2 to CH_4 is achieved through low flowrates (~3 ml min⁻¹ of CO_2)





and thus, low space velocities when considering the weight of the Ni-based electrode, while hydrogen feedstock was used instead of steam. To address the former issue, a combination of the above approaches would be beneficial by introducing a heterogeneous catalyst bed in the PCMR, in a similar manner to what has been shown previously in ceramic electrolyte membrane reactors for methane activation [34, 75, 93, 94]. By introducing a catalyst bed, hydrogen is evolved over Ni cermet and subsequently it reacts with the carbon-containing molecule over the catalyst bed, circumventing the need for reinventing the MEA. A similar approach can also aid other systems of equilibrium reactions with decreased product volume favored by pressurization, such as ammonia synthesis and possibly higher hydrocarbon formation from CO/CO₂ mixtures. In addition, for the ideal case where H₂O is the hydrogen feedstock, efficient and stable OER electrocatalysts exhibiting high performance (>0.5 A cm⁻²) close to 400 °C–450 °C, such as the calcium-cobalt misfit layered, and the double perovskites discussed in the steam electrolysis section may answer these challenges.

Dehydrogenation of ethane or methane to C_2 s is a concept is of crucial importance due to the wide use of ethylene in the production of polymers. The interesting aspect is that the reaction of an alkane towards alkenes (e.g. ethane to ethylene) constitutes a partial oxidation reaction when air is fed to the cathode, and thus, creates a significant electromotive force (>0.9 V at 700 °C) for the cogeneration of power. Of course, the alternative could have as target the production and in-situ recovery of hydrogen when no air is supplied to the cathode. The idea of chemical cogeneration [13] of electrical power is a rather intriguing aspect of EMRs. The concept was first proposed by Vayenas [95], while later it was applied by several research groups. Nevertheless, when dealing with dry hydrocarbon systems, the major issue is coking. So far, several pioneering works have proposed solutions with stable perovskite anodes during ethane dehydrogenation to ethylene with high yields and selectivities, while maintaining adequate stability for >100 h.

SOEC systems commonly operate with gas reactants and products due to the high temperatures involved. There are of course some special cases such as the direct carbon (solid or in molten carbonates) fuel cells with different coals as feedstock, but such approaches with fossil fuels cannot be considered anymore sustainable. The substitution of coal with solid biomass could tackle these issues, but the high gasification rates of biomass at temperatures above >500 °C due to the high content of volatile matter, imposes complexity and thus, critical engineering challenges for gas recirculation towards the exploitation of the overall energy content of the fuel feedstock. To this direction, the SoA PCMRs could open new horizons for the direct utilization of bio-based solid feedstocks as has been shown by Kyriakou *et al* [45]. In this work [96], a tubular Ni-BZCY configuration was proposed to achieve hydrogen production and recovery from steam gasification of carbon black (99% pure carbon at 600 °C and atmospheric pressure. An alternative would be the swap of the feedstock to biomass (e.g. biochars) or waste, in order to take advantage of the temperature compatibility of the gasification process and high protonic membrane flux towards in situ hydrogen recovery (or pressurization as well), pure CO₂ for CCUS by exploiting the overall heat content of a low-cost renewable source or waste.



4.6.3. Circumventing dead ends with new strategies

A wider deployment of the PCMRs in the coming years will put forward several applications related to direct electrified synthesis. Various reaction schemes may integrate highly complex processes with electrode properties beyond Ni-BZCY will necessitate the reinvention of the membrane-electrode assembly and its design. For instance, the ammonia synthesis from steam and nitrogen will require the development of Ni cermet-free electrodes since the current Ni cermets favor the side HER when used as cathodes or are oxidized when used as anodes for OER. Therefore, this will require new PCMR configurations as shown in figure 9, with cells beyond electrode-support through, for instance, the introduction of an independent porous backbone to act as support for the new MEA [97]. Other examples for the need of new designs is related to the production of hydrocarbons from CO or CO₂ due to the simultaneous production of steam that limits the system and increase its complexity. The use of co-ionic membranes that consist of protonic ceramic and oxygen ion conducting could increase the utilization of the current (i.e. better FE) since the H₂O produced can be concurrently electrolyzed in the same electrode, and thus, the present systems should be re-engineered. The preparation of the electrolyte in this case would be challenging, however, Ivanova *et al* [98] proposed a solution by constructing a BaCe_{0.8}Eu_{0.2}O₃₋₆:Ce_{0.8}Y_{0.2}O₂₋₆ dual phase electrolyte.

Dinitrogen fixation is by far the most challenging electrochemical reaction that has been studied in PCMRs. To carry out this reaction at higher temperatures offers a unique advantage due to the enhanced kinetics for the endothermic cleavage of the dinitrogen triple bond. In addition, the demonstration of metal nitrides (or oxynitrides) as electrocatalysts could offer a new alternative in the field of electrocatalytic research. Advanced modeling studies and experimentation should be combined towards understanding the underlying cathode processes at nanoscale in order to demonstrate significantly improved faradaic efficiencies and reaction rates to ammonia. Certainly, the targets for the process regarding feasibility as set by Giddey *et al* about a decade ago, and confirmed by the DoE in US, cannot be reached in a blink of an eye. There is, however, an urgency for a drastic increase in the reported rates and faradaic efficiencies that would offer some boost to the technology. For instance, expanding DFT modeling to prediction of new electrocatalysts beyond liquid electrolyte systems [99], dedicated to higher temperatures whereby PCMR operate could be a solution. Other alternatives could be the increase in the reactor pressure to suppress HER [38] or the hybrid plasma-PCMR approach proposed by Sharma *et al*, in which FEs up to 88% were reported. For the latter of course, some detailed energetic analysis should be performed in order to elucidate the actual energy efficiency of this hybrid system.

Finally, ammonia production with high FEs can be also expected when the nitrogen source is not atmospheric dinitrogen, as for instance in NO_x reduction. In this case, the nitrogen already exists in its atomic form, thus eliminating the challenging dinitrogen triple bond cleavage and rendering its hydrogenation much simpler. A similar approach has been successfully demonstrated in low temperature electrochemical systems with nitrate source with promising results [100]. Although very attractive, this route should be not considered as a direct alternative to technologies utilizing the abundant atmospheric dinitrogen, such as the HB process and the electrocatalytic dinitrogen fixation, since NO_x feedstock is not

equally abundant. Nonetheless, it would be interesting to explore this reaction scheme in PCMRs by starting from the evaluation of electrocatalytic activity and stability of the SoA Ni cermets in the presence of the oxidizing NO_x species.

5. Conclusions

PCMRs constitute an exciting platform for electrification processes with high potential in terms of efficiency and flexibility. During the last few years, significant progress has not only been made on the cell components, but also on increasing the readiness level through scaling project demonstration. Among the explored technologies, the production of pressurized hydrogen from sustainable sources, such as biogas and ammonia, seems to be closer to commercialization, while significant steps forward have been made in the generation of green hydrogen from steam electrolysis. Other processes, such as CO₂/H₂O co-electrolysis, hydrocarbon conversion and ammonia synthesis have been successfully demonstrated by showing promising results, albeit with challenges related to the FE and stability of the systems. Therefore, the efforts should focus beyond the experimental discovery of materials, e.g. on multiscale modelling that would aid optimization of the electrode, electrolyte and their interface, as well as their operating conditions towards enhancing the economic viability of electrosynthesis with PCMRs. Anyhow, the combination of increased number of reported achievements and the necessity of developing sustainable energy storage as well as chemical industry electrification technologies has built an unprecedented momentum for PCMRs which should be capitalized in order to assess their actual capabilities.

Data availability statement

No new data were created or analysed in this study.

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