Position Paper

Hydrogen Europe Research

Challenges in Manufacturing

Structurally Stable Ceramic Membranes

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Abstract

Structurally stable ceramic membranes are pivotal for advancing hydrogen technologies, enabling efficient energy conversion, separation, and chemical processing under demanding conditions. Despite their superior thermal, chemical, and mechanical resilience, the large-scale deployment of ceramic membranes remains constrained by significant manufacturing and mechanical stability challenges. Key limitations include defect formation during shaping and sintering, multi-layer co-sintering issues, porosity control across multiple length scales, and brittleness under thermal and mechanical loads. This position paper analyzes these challenges, emphasizing the critical interplay between material composition, microstructure, macro-geometry, and processing strategies. We highlight emerging solutions, including multi-phase ceramic composites, high-entropy oxides, graded and hierarchical porous structures, advanced macro-geometries, and hybrid manufacturing approaches integrating additive manufacturing with conventional techniques. Furthermore, the integration of multi-scale modeling and AI-driven material design offers a pathway to accelerate the discovery of high-performance, durable membranes while optimizing fabrication protocols. By addressing both material and process innovations, this work provides strategic guidance for developing next-generation ceramic membranes tailored for hydrogen applications, supporting durable, efficient, and scalable hydrogen technologies.

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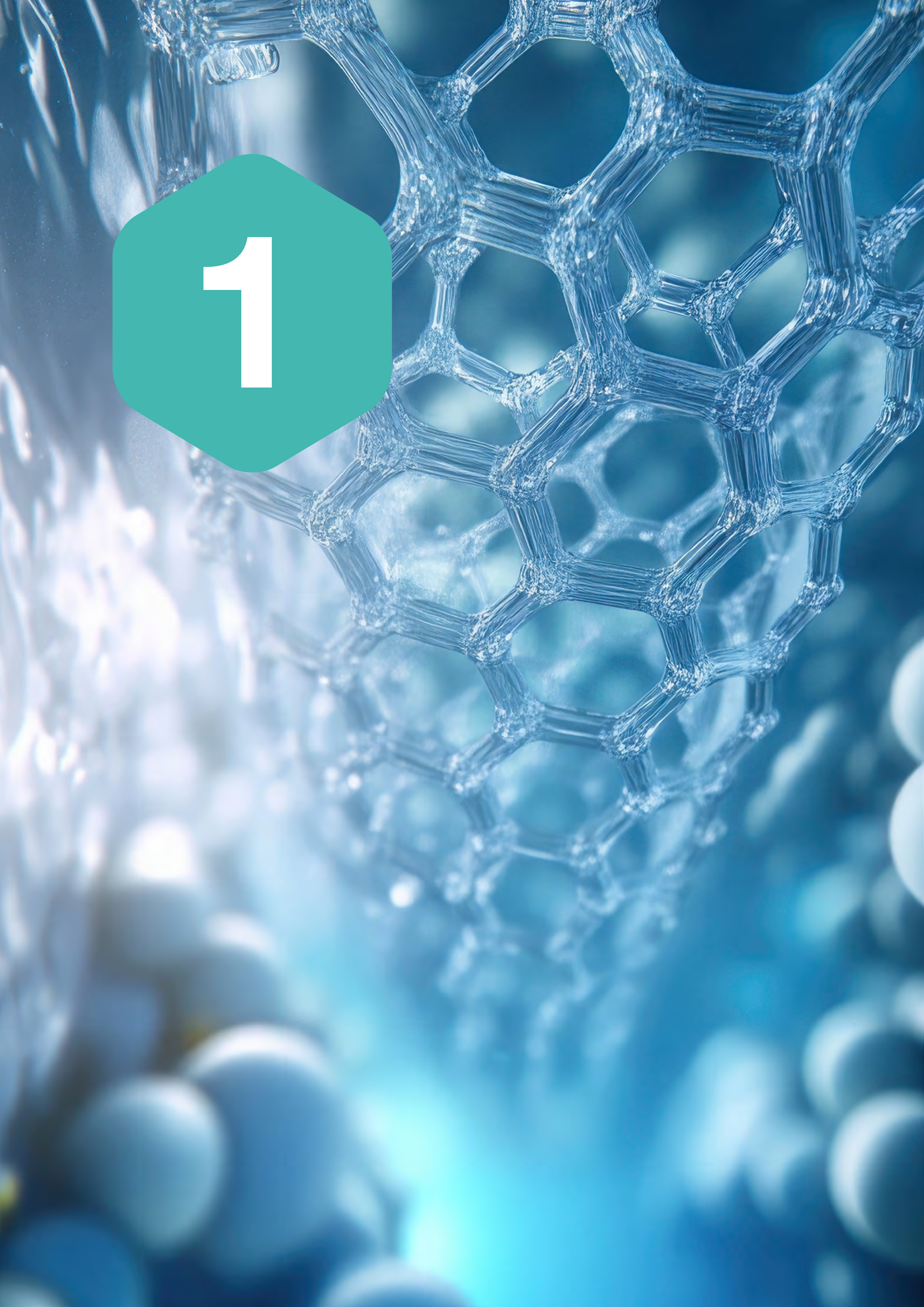
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Introduction

The development of structurally stable membranes is crucial for advancing hydrogen technologies in Europe, enabling efficient energy conversion, separation, and chemical processing. Ceramic membranes stand out for their thermal and chemical stability, tailored selectivity, and efficient transport properties (permeability, ionic or mixed ionic-electronic conductivity), making them ideal for electrochemical applications and increasingly relevant in selected pressure-driven processes. Their enhanced structural integrity - and, in some cases, engineered multiscale porosity ranging from nano- to micro- and mesopores - further supports advanced functionality across diverse hydrogen-related applications, including production, purification, energy conversion, and storage. In fuel and electrolysis cells, as well as catalytic reactors and separation systems, structurally stable membranes with tailored gas-tightness or controlled porosity improve performance and extend longevity, benefiting stationary and mobile power generation and enhancing hydrogen or chemicals production efficiency. Pore architecture enables selective hydrogen extraction, improves reforming yields, and contributes to energy savings and process sustainability. Integrated into industrial systems and energy storage platforms like power-to-gas, ceramic membranes support grid stability and promote the widespread adoption of hydrogen as a clean energy carrier.

Despite their advantages, the large-scale deployment of ceramic membranes is constrained by significant manufacturing and mechanical stability challenges, which directly impact their reliability, efficiency, and cost-effectiveness. Achieving structurally stable membranes remains a key challenge in next-generation hydrogen technologies. Manufacturing processes like shaping, casting, additive manufacturing, sintering, and co-sintering often introduce defects, porosity variations across scales, and residual stresses, leading to mechanical failure and compromising gas-tightness, ionic conductivity, and durability. Additionally, ceramic membranes are prone to cracking, delamination, and thermal expansion mismatches, especially under thermal cycling, mechanical loads, and steam exposure, limiting their real-world applicability in hydrogen systems.

This position paper aims to analyze the key challenges in manufacturing structurally stable ceramic membranes for hydrogen applications, focusing on both material and process limitations. It presents an overview of ceramic membrane materials, highlights key manufacturing and mechanical stability challenges, and underscores the pivotal role of multiscale porosity in enabling high-performance operation. The exclusive focus on ceramic membranes is warranted by their exceptional thermal, chemical, and mechanical robustness, which renders them uniquely suitable for high-temperature and harsh-environment conditions. By contrast, alternative membrane types - such as polymeric or AgPd membranes - are already well established, with mature manufacturing routes and proven performance in low-temperature applications. Including such membranes would unnecessarily broaden the scope and dilute the technical depth dedicated to ceramics. The paper emphasizes the need for innovative solutions and reinforcement strategies, including new material compositions, optimized porous architectures, advanced macro-geometries, etc., to improve membrane durability and performance. By addressing these aspects, it provides expert insights to accelerate innovation, shape research priorities, and offer strategic recommendations for EU research initiatives, fostering multidisciplinary collaboration and stronger industry-research partnerships.

2

Overview of Ceramic Membrane Materials for Hydrogen Applications

Membrane material selection is a critical determinant of performance, durability, and manufacturability in hydrogen technologies - and is ultimately dictated by the specific application. Selecting the appropriate material ensures high efficiency, long-term stability, and scalable production, making it central to next-generation hydrogen systems[1,2]. Ceramic membranes are typically based on ionic conductors (oxygen-ion, proton, co-ionic)[3], mixed ionic-electronic conductors[4], or porous ceramic structures[5], each offering distinct transport or separation properties suited to specific operational demands.

- Oxygen ion conductors (e.g., Yttria-Stabilized Zirconia (YSZ), Gadolinia-Doped Ceria (GDC)) enable oxygen ion transport at elevated to high temperatures (≥700 °C for YSZ; ≥550 °C for GDC) and are widely used in solid oxide fuel and electrolysis cells (SOFCs/SOELs).

- Proton-conducting ceramics (e.g., Y-substituted $BaZrO_3$/$BaCeO_3$ (BZCY), $La_{5.5}WO_{12-\delta}$ (LWO)) enable proton transport at intermediate to elevated temperatures (400-650°C), making them suitable for protonic ceramic fuel and electrolysis cells (PCFCs/PCCELs), electrochemical membrane reactors, hydrogen pumps.

- Co-ionic conductors (e.g., $BaCe_{0.5}Zr_{0.3}Y_{0.2}O_{3-\delta}$ perovskites, $Ba_7Nb_4MoO_{20}$-based perovskite-related oxides) enable simultaneous oxygen ion and proton conduction, offering unique advantages for membrane reactors and electrochemical devices operating in mixed gas environments or under steam (reforming, co-electrolysis, chemical looping).

- Mixed ionic-electronic conductors (MIECs) (e.g., perovskite-based materials such as LSCF ($La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$), BSCF ($Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$), LWO) combine electronic conductivity and oxygen-ion or proton conductivity, making them ideal for pressure-driven oxygen or hydrogen separation processes and membrane reactors.

- Porous ceramic membranes (e.g., alumina, silica, titania) offer high surface area, tunable porosity, and excellent thermal and chemical resistance, making them suitable for demanding applications. They are widely employed in hydrogen purification and as membrane reactors for processes such as steam methane reforming (SMR), ammonia decomposition, and the water–gas shift (WGS) reaction. In addition, advanced materials like graphene and ceramic–graphene composites are increasingly explored to enhance permeability and selectivity. Functional layers (e.g., palladium-based or proton-conductive coatings) further enable selective transport and catalytic conversion, supporting hybrid concepts that integrate separation and reaction in a single step.

Material properties such as thermal stability, mechanical integrity, electrical conductivity, hydrogen flux, chemical resistance etc., vary significantly across ceramic membrane classes, directly influencing their suitability for specific hydrogen applications. As outlined in Table 1, key limitations, including challenging processability, moderate mechanical strength, and low reproducibility, continue to hinder the development and large-scale deployment of structurally stable membranes.

Table 1. Comparative overview of major types of ceramic membranes, including graphene-based porous membranes, relevant to hydrogen applications, emphasizing performance trade-offs and key fabrication challenges affecting structural stability, scalability, and industrial deployment.

Membrane Type	Stability			Conductivity	Manufacturing			Key applications
	Therm.	Chem.	Mech.		Process-ability	Reproduci-bility	Scala-bility	
Oxygen ion conductors	H	M to H	H	M to H (O^{2-})	Good	H	H	SOFCs, SOECs, Membrane reactors
Proton conductors	M	M	M	M to H (H^+)	Challenging	L to M	L to M	PCFCs, PCCELs, Membrane rectors, Hydrogen separation, purification, sensors, pumps, Hydrogen recovery
Co-ionic conductors	M to H	M	M	M to H (O^{2-}, H^+)	Challenging	Under develop-ment	Emerging	Membrane reforming, co-electrolysis, chemical looping
MIECs	M	L to M	M	H (O^{2-}, e^-) M (H^+, e^-)	Moderate to Good	M	M	Membrane reactors, oxygen/ hydrogen separation
Porous (e.g., based on graphene, alumina, silica, titania)	M to H (M, H, M, M to H)	M to H (H, H, M, H)	H (VH in plane, H, L to M, M)	Not applicable	Excellent (Challenging, E, good but brittle at high T, good)	H (L, H, M, M to H)	H (L to M, H, M, M to H)	Hydrogen purification, separation, (nano)-filtration, pervaporation, catalytic membrane reactors, sensing

VH: very high; H: high; M: moderate; L: low.

The specified material-related limitations, alongside critical raw material dependency and complex manufacturing requirements, underscore the urgent need for innovation in membrane design and processing. The following chapter examines these challenges in detail, with a focus on structural optimization, scalable fabrication methods, and sustainable material strategies to enable next-generation hydrogen membrane technologies. Future progress will depend on optimizing material compositions, tailoring microstructures, and advancing fabrication techniques to enhance both performance and scalability in industrial hydrogen applications.


3

Current Challenges in Manufacturing: Formulation, Shaping and Processing

Manufacturing structurally stable ceramic membranes is hindered by a set of interconnected challenges spanning formulation, shaping, and processing. A critical difficulty lies in **controlling porosity across multiple length scales**, which is essential for enabling gas transport, mechanical integrity, and functional performance. The widespread use of pore-forming agents adds complexity and introduces risks such as swelling, gas entrapment, and residual impurities, all of which compromise membrane performance. In parallel, **defect formation during thermal treatment** (drying, sintering), such as warping, delamination, or cracking, commonly results from poor green strength and inhomogeneous shrinkage, while many advanced functional ceramics exhibit **limited formability or poor phase compatibility**, further complicating their shaping. Conventional methods like tape casting and extrusion struggle with achieving **geometric precision and scalability for complex architectures. Additive manufacturing** (AM) offers a promising route for fabricating membranes with integrated porous-dense domains and tailored geometries, but it remains **immature for thin, functional ceramics**. Key limitations include low resolution, slow build rates, and limited material compatibility, while high costs and lack of standardization in post-processing continue to hinder industrial adoption. Moreover, the absence of robust hybrid workflows that combine the scalability of conventional techniques with AM's design flexibility, alongside unresolved reproducibility issues, further delays scale-up. Beyond th**ese, additional shaping-related issues further constrain progress. Rheological control** of ceramic slurries or pastes is critical during casting and printing; poor dispersion, viscosity instability, or particle sedimentation can lead to film inhomogeneity, edge defects, and local stress accumulation. Likewise, in multilayer membrane architectures, ensuring **interlayer compatibility during green processing (i.e., in the unsintered state)** is essential to prevent delamination, interfacial stress, or mechanical failure prior to sintering. In addition to the previously outlined issues, further formulation and shaping-related challenges continue to constrain the reliable production of ceramic membranes. An improperly optimized particle size distribution can result in poor **packing density and local inhomogeneities** in the green body, undermining both mechanical stability and porosity control. In additive manufacturing, the formulation of printable ceramic inks or pastes remains a bottleneck; achieving the required rheological properties without compromising extrusion stability, layer adhesion, or feature resolution is a complex task. Moreover, during tape casting or direct deposition, **interaction with**

carrier substrates frequently causes film tearing, wrinkling, or edge defects upon release, particularly in ultra-thin or large-area membranes. **Environmental factors** such as ambient humidity and temperature also exert a strong influence on slurry behavior, drying kinetics, and green body uniformity, requiring tightly controlled processing conditions to avoid variability and defect formation. **Sintering** is a crucial step in ceramic membrane fabrication, playing a key role in achieving dense, defect-free structures with the necessary mechanical strength, optimized ionic conductivity, and gas-tightness. Through high-temperature treatment, sintering enables particle bonding and densification, reducing porosity and enhancing structural integrity. However, improper sintering can lead to excessive or uncontrolled grain growth, microcracking, or residual stress accumulation, severely compromising membrane performance. Achieving optimal sintering conditions requires precise control of temperature, heating profile, and atmosphere to balance densification and mechanical stability. Too low a temperature results in **insufficient densification**, leading to poor mechanical strength and high permeability, while excessively high temperatures can cause over-sintering, grain growth, or phase decomposition, ultimately reducing thermal and chemical stability. Furthermore, different ceramic compositions exhibit varying sintering kinetics, making it challenging to define a universal sintering protocol applicable to all materials used in hydrogen-related applications. An even greater challenge arises in **co-sintering**, which is required for multi-layered ceramic membranes that combine functional layers with different compositions, microstructures, and properties. Integrating several ceramic layers requires precise control over shrinkage rates, thermal expansion mismatches, interface stability, and sintering compatibility. If these factors are not carefully managed, co-sintering can lead to delamination, interfacial defects, segregation of undesired secondary phases, or residual stress-induced cracking, reducing both mechanical stability and functionality. To overcome these challenges, advancements in sintering aids, optimized thermal profiles, and alternative densification methods such as electric field-assisted sintering, cold (aka hydrothermal) sintering and light-assisted (e.g., laser) sintering are being explored. These techniques offer improved densification, phase content and grain size control, reduced sintering times, and enhanced interfacial bonding, providing promising solutions for manufacturing robust, high-performance ceramic membranes for hydrogen applications. Digital approaches (e.g., finite element modeling, phase-field simulations, machine learning) simulating the evolution of properties during the sintering process, alongside a systematic set of experiments for validation, would further accelerate developments in the field.

Beyond the control of the material's composition and structure, the manufacturing process itself also requires improvements. Processing of ceramics is in general a laborious, multi-step, time- and energy-intensive process, and thus rather inefficient and costly. New sintering technologies hold great promise to boost the efficiency of these manufacturing processes, while offering additional process parameter space for better tuning of the membranes' performance. The majority of these technologies is, however, still requiring research and development.

These combined challenges underscore the need for integrated solutions that bridge material formulation, advanced shaping strategies, precise process control, and digital approaches, laying the groundwork for scalable, high-performance ceramic membranes for hydrogen technologies.

To accelerate progress, it is crucial to merge the established expertise of traditional shaping techniques, such as tape casting and extrusion, known for their scalability and reliability, with the design flexibility and geometric precision offered by additive manufacturing and emerging sintering techniques. This integrative approach enables the co-fabrication of complex architectures, graded porosity, and multi-functional membrane structures, offering a more effective pathway toward scalable, cost-efficient production tailored to next-generation hydrogen applications.


4

Current Challenges in Mechanical Stability of Manufactured Membranes

Ceramics are intrinsically brittle, a characteristic that often limits their structural applications unless specific toughening mechanisms are intentionally incorporated. One such case relevant for ceramic membranes is yttria-stabilized zirconia (YSZ), which can achieve enhanced toughness at intermediate Y-doping levels (partially stabilized zirconia). However, most ceramics used in membrane technologies remain highly susceptible to cracking. The complex geometries and demanding operating conditions of ceramic membranes expose them to mechanical failure during both fabrication and service.

During processing, critical steps such as drying, binder and pore former removal, and especially sintering can introduce cracks, voids, and delamination. These defects typically arise from mismatches in shrinkage rates across the different layers of the membrane structure, leading to localized stress concentrations at their interfaces. In operation, additional challenges include mismatches in thermal expansion coefficients and the accumulation of thermomechanical fatigue, which can lead to cracking and delamination.

Such vulnerabilities significantly limit the operational lifespan and reliability of ceramic membranes, preventing them from reaching their full potential in terms of durability and service temperatures. To address these limitations, robust mechanical characterization methods are essential. However, testing the thermomechanical stability of ultrathin, brittle membranes presents its own set of challenges. In situ testing techniques that capture behavior across multiple length scales are especially valuable, as they help identify the critical scale at which failure originates and propagates. Tools such as digital image correlation and high-temperature in situ mechanical testing, combined with advanced simulations that account for fracture, are also instrumental.

There is a general need for a comprehensive redesign of ceramic membranes for hydrogen applications, addressing both macroscale geometry and mesoscale (microstructural features at the 1–100 µm scale) architecture (microstructural features at the 1–100 µm scale) architecture to reduce stress concentrations. At the same time, there is a growing demand for standardized, reliable, and accessible mechanical testing protocols to guide material development and ensure performance consistency.


5

Call for New Compositions, Porous Structures, Macro-Geometries and Manufacturing Strategies

To overcome the structural and mechanical limitations of ceramic membranes in hydrogen applications, advancements in material composition, porosity engineering, and geometric design are essential. Novel material compositions, optimized porous structures, and innovative macro-geometries can significantly enhance mechanical stability, durability, and overall membrane performance. New and hybrid manufacturing techniques also need to be envisioned to enable the realization of such innovative material concepts. Furthermore, multi-scale modeling and AI-driven material design present new opportunities for accelerating the development of high-performance membranes tailored to specific operational conditions.

5.1 Novel Material Compositions for Enhanced Structural Stability

Current ceramic membranes suffer from fracture susceptibility, thermal expansion mismatches, and chemical degradation, particularly under cyclic thermal and mechanical loads. The development of multi-phase ceramic composites, such as perovskite-based proton conductors reinforced with high-strength oxides (e.g., $BaZrO_3$-ZnO or BCZY-Al_2O_3 composites), can enhance mechanical resilience. Similarly, graded materials with transition layers between different phases can help reduce stress concentrations and improve overall durability. Alternatively, engineering the interfaces between the membrane layers has high potential to minimize structural stability issues. Further reinforcement strategies, including fiber- or whisker-reinforced ceramics, nanostructured composites, or glass–ceramic hybrids, could provide additional toughness and thermal shock resistance.

Moreover, doping strategies can be optimized to balance ionic conductivity and mechanical strength. For example, rare-earth doping in zirconates and cerates enhances both proton mobility and chemical stability, reducing degradation in CO_2- and H_2O-rich environments. The integration of high-entropy oxides (HEOs) is another promising avenue, as these materials offer superior phase stability, reduced grain growth, and tunable ionic conduction properties. In addition, multi-cation perovskites, fluorite-type oxides, and defect-engineered solid solutions represent attractive design directions for combining chemical robustness with enhanced transport performance.

5.2 Porous Structures for Improved Mechanical Integrity

Porous architectures play a crucial role in balancing mechanical strength and functional performance, especially in composite and multi-layered membranes. Tailoring porosity at multiple scales - nano, micro, and meso - can help mitigate thermal stress buildup, enhance gas diffusion, and prevent mechanical failure. Tunable multiscale porosity can offer fine control over gas permeability, transport properties, stress distributions, fracture behavior, and thermal expansion mismatches.

New processing techniques, such as freeze casting (ice templating), colloidal assembly, scaffold 3D-printing, and sacrificial templating, enable precise control over pore size distribution and connectivity, showing great potential to improve both mechanical stability and performance in hydrogen applications.

5.3 Innovative Macro-Geometries for Performance Stability

Beyond material composition and porosity, macro-structural design plays a key role in improving mechanical resilience and operational stability. Traditional flat-sheet membranes often suffer from stress concentration and structural fragility, whereas engineered geometries can better accommodate thermal and mechanical stresses.

- Honeycomb structures distribute mechanical loads more evenly, reducing stress points and improving durability.
- Tubular configurations enhance thermal shock resistance and scalability for large-scale applications.
- Non-flat (wavy or roughened) interfaces prevent stress concentrations and promote interlocking.

- Layered architectures with graded porosity optimize both gas diffusion and structural support, enhancing long-term performance.

AM and advanced ceramic shaping techniques allow the fabrication of complex geometries, offering new possibilities for multi-functional membrane designs tailored for specific hydrogen applications.

5.4 New and Hybrid Manufacturing Methods

New and hybrid manufacturing methods hold great promise to overcome the limitations of casting and production of membranes with a discrete number of layers, with limited control over their nano- and microstructures.

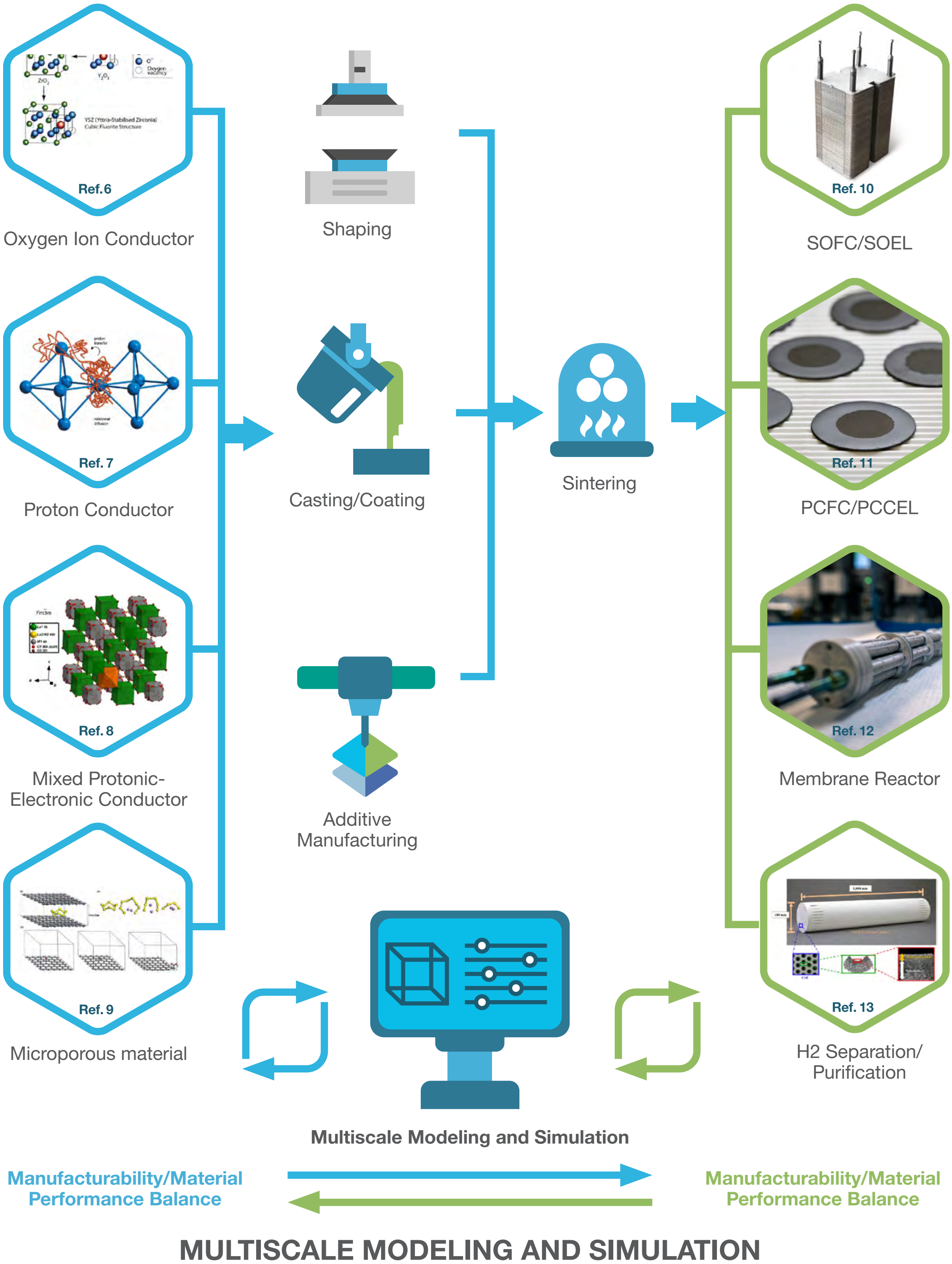
AM enables the fabrication of novel meso- and micro-scale geometries that enhance structural integrity, optimize gas permeability, and improve material efficiency. A wide array of AM techniques is now being explored for ceramic processing. These include material jetting, known for its high resolution and versatility albeit slower speed; binder jetting, which offers scalability and broad material compatibility despite lower resolution; and material extrusion or direct writing, which provide cost-effective and flexible solutions with moderate precision. Vat photopolymerization, although still immature for many ceramic compositions, can deliver very high resolution.

In parallel, advanced nano- and micromanufacturing methods such as colloidal assembly, templating, and freeze casting are increasingly used to introduce hierarchical porosity with great precision. These methods contribute to improved mechanical performance through the development of geometries that optimize stress distribution, and they even allow the incorporation of toughening mechanisms.

At the densification stage, innovative sintering technologies that rely on solvents (cold sintering), electric fields and currents (Field-Assisted Sintering Technique/Spark Plasma Sintering (FAST/SPS); Ultrarapid-High-temperature Sintering, (UHS), flash sintering), lasers (selective laser sintering) or light (photonic sintering, blacklight sintering) provide a new level of control over structural evolution. By tailoring heating rates and mass transfer mechanisms, these approaches allow multiscale manipulation of membrane architectures, preserving the intricate features created during earlier processing stages.

To fully exploit these capabilities, it is essential to adapt and integrate these advanced manufacturing and sintering techniques into the underutilized ceramic materials required for specific hydrogen-related functionalities.

Figure 1. Integrated approach for the fabrication and performance optimization of ceramic membranes for hydrogen applications. This depiction highlights examples and does not represent all possible materials, technologies, or final products.



5.5 The Potential of Multi-Scale Modeling and AI-Driven Material Design

The integration of multi-scale modeling and AI-driven material design can accelerate the discovery of new compositions and structures while optimizing their manufacturing feasibility. Machine learning algorithms can rapidly analyze large datasets to predict optimal dopant concentrations, microstructural configurations, and mechanical performance under various conditions. Computational simulations, such as finite element analysis (FEA) and density functional theory (DFT), can guide design choices before experimental trials, reducing development time and costs. Multiscale and multiphysics modeling can also capture the manufacturing processes, and efficiently streamline experiments, allowing the gaining of new insights in the driving process parameters, and a significant decrease of time- and energy-intensive experimental campaigns. An integrated approach of those digital tools with experimental validation and shared collection of measured data on material properties and resulting performance would aid an acceleration of material development.

By leveraging novel materials, tailored porosity, innovative macro-geometries, and computational design tools, the next generation of ceramic membranes can achieve unprecedented structural stability, efficiency, scalability, paving the way for durable and high-performance hydrogen technologies (Fig. 1).

6

Conclusions and Recommendations

To overcome the challenges of ceramic membrane fabrication, novel material compositions, optimized multi-scale porosity, and innovative macro-geometries are essential. These advancements will enhance the mechanical stability and performance of membranes for hydrogen technologies.

Material Composition and Structural Design: A critical analysis of the currently used materials, plus the exploration of multi-phase ceramic composites and high-entropy oxides can provide paths to improve mechanical resilience while maintaining high functional performance. Engineering the interfaces between layers and employing graded materials can help mitigate structural instability and thermal expansion mismatches.

AM Potential: The integration of AM with traditional shaping techniques and nano/micromanufacturing methods can allow for more precise control over membrane architecture, enabling the creation of complex geometries and tailored porosity at nano, micro, and meso-scales.

Improved Co-Sintering Methods: New sintering technologies offer more flexibility and control in densification processes. These methods can better preserve the intricate features introduced by AM and nano/microstructuring techniques, while preventing cracking and delamination issues during fabrication.

AI and Multi-Scale Modeling: Leveraging AI-driven material design and multi-scale modeling will accelerate the development of new materials and optimize manufacturing processes. These tools can predict optimal compositions and processing conditions, reducing trial-and-error experimentation and speeding up the material development cycle.

Future Research and Collaboration: The successful realization of durable, high-performance ceramic membranes for hydrogen applications will require ongoing collaboration between academia, industry, and policy-makers, for the definition of common relevant research ambitions and supporting out-of-the-box, fundamental research ideas[14]. Multidisciplinary efforts will be key to addressing the manufacturing and stability challenges that hinder widespread adoption, while a coordinated, cross-sectoral approach will be vital to unlock the full potential of ceramic membrane technologies in the hydrogen economy.

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