

Challenges and Future Prospects in Perovskite-Based Fuel Cells: A Comprehensive Review

Abstract

The remarkable ionic conductivity of the perovskites oxides, the ability to adjust its crystal structure, and its electrocatalytic capability have compelled perovskite oxides to get a prospective in to become a personal family of materials of next generation fuel cells. Their overall structure, ABO₃, allows substituting cations at either the A - or B -sites, making it possible to control precisely redox stability, electrical conductivity, and oxygen vacancy concentration. In both solid oxide and proton-conducting fuel cells, these properties of the perovskites render it attractive as a cathode (such as La_{1-x}Sr_xCo_{1-y}Fe_yO₃), anodes (such as SrTi_{1-x}Fe_xO₃), and electrolytes (such as BaCeO₃, BaZrO₃ systems). Recent tests illustrate how composite designs, defect engineering and nanostructuring can enhance proton transport, reduce strontium segregation as well as oxygen reduction kinetics. Nevertheless, such challenges as limited work efficiency in mid temperatures, scalability of synthesis, and long-term chemical instability at CO₂/H₂O coordinates remain great setbacks. In this review, the future development of viable, durable, and cost-effective perovskites fuel cells is provided through the review of the structural design methods, mechanism, and current perovskite fuel cell technology development.

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Received on: 10.08.2025

Revised on: 22.08.2025

Accepted on: 30.08.2025

Keywords: Perovskite materials; Fuel cells; Oxygen ion conductivity; Electrochemical performance; Energy conversion.

Introduction

Studies on fuel cell, which is famously characterized by high efficiency, flexibility with fuel accompanied by eco-friendly activities, intensified due to increasing need of environmentally friendly and sustainable energy technologies globally. Fuel cells may run on a variety of fuels and reduce greenhouse gas emissions by directly converting chemical energy in electrical power, in contrast to conventional combustion-powered systems (Steele et al., 2001 and O' Hayre et al. 2016) Due to the fact that solid oxide fuel cells (SOFCs) as well as proton-conducting fuel cells (PCFCs) directly convert chemical energy into electrical power, whereas the other varieties rely on combustion, fuel cells have received a lot of interest. Still, developing high-performance electrode and other materials such as electrolytes remain a big challenge in the way toward long-life half-cost fuel cell solutions. Perovskite oxides (general formula ABO₃) a wide category of useful fuel cell materials have become popular.

Either the A-site (rare earth as well as alkaline earth metals), or the B-site (transition metals) can be used for substitution; this allows for precise customization of physicochemical properties like oxygen vacancy concentration, ionic conductivity, electronic conductivity, as well as catalytic activity (Goodenough et al., 2007, Skinner et al., 2001, and Li et al., 2021). The tunability of perovskites renders them valuable electrolytes (e.g., BaCeO₃, BaZrO₃-based systems), anodes (e.g., SrTi_{1-x}Fe_xO₃, La_{0.7}Sr_{0.3}Cr_{0.5}Mn_{0.5}O₃), and cathodes (e.g., Sr_{1-x}Co_{0.8}Fe_{0.3}O₃, Ba₀, Ba_{0.3}Sr_{0.5}Co_{0.8}Fe_{0.3}O₃, Ba_{0.3}, Ba_{0.7}Fe_{0.3}O₃, Ba_{0.0.0.0.0.0.8}Fe_{0.8}Fe_{0.8}Fe_{0.8}Fe_{0.0}).

Recently, defect engineering, nanostructuring, and even the compositing methods have been subject to improvement to reduce long-standing issues such as strontium segregation, coking, a slow oxygen reduction reaction, and even the instability during the carbon dioxide and water environments (Porotnikova et al., 2024, Laguna et al., and Li et al., 2020). The progress in making protons conduct perovskites has also enabled the usage of fuel cells in intermediate operating temperatures (400-700 degrees Celsius) which has reduced the cost of operation yet did not compromise on the performance (Rehman et al., 2024). These developments notwithstanding, chemical stability, scalability of synthesis and long term durability are key barriers to commercialization.

This paper provides a general overview of the structural features, electrochemical properties and applications of the perovskite oxides in fuel cells. We sketch the future in terms of developing reliable and effective perovskite fuel cells, illustrate the inherent difficulties, and provide an overview of the recent developments in perovskite-based cathodes, anodes, and electrolytes.

2. Structure and Properties of Perovskites

The general chemical formula for perovskite oxides is ABO₃, where the A-site cation is usually a bigger rare-earth and alkaline-earth metal (like La³⁺, Sr²⁺, or Ba²⁺) and the B-site cation has a smaller transition-metal (like Mn^{3+/4+}, Fe³⁺, Co³⁺, or Ti⁴⁺). At the ideal cubic perovskite structure, the oxygen anion at the face centers, the B-site cation at the body center, as well as the A-site cations at the unit cell's corners form an octahedral network (Muller et al., 1974 ; Howard et al., 2005). With goldschmidt tolerance factor (*t*), ionic size mismatch often results in deviation of the ideal cubic symmetry such as orthorhombic or tetragonal distortions.

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$

In which the ionic radii of A, and B, along with the radii of oxygen is expressed by *r*_A, *r*_B, and *r*_O, respectively. While aberrations show irregularities in the distribution and have a significant impact on the electrochemical characteristics of perovskites, the tolerance factor is around unity, suggesting that their distribution is stable as well as cubic in nature (Goldschmidt et al. 1926).

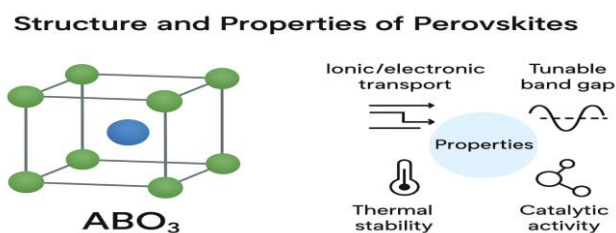


Figure 1. Structure and Properties of Perovskites

2.1 Ionic and Electronic Conductivity

One of the most important features of the perovskites relevant to fuel cell applications is mixed ionic-electronic conductivity (MIEC). Oxygen vacancies are formed by a replacement of the A-site by negatively charged cations (say with Sr^{2+} replaced by La^{3+}) in order to maintain charge neutrality and enhance oxygen diffusion. The numerous oxidation states, which B-site transition metals are able to undergo, further promote the conduction of electrons or holes (Steele et al., 2001 and Skinner et al., 2001). Because of these properties, perovskites are particularly highly suited to purpose as anodes in hydrocarbon-fueled systems, and as cathode materials in the oxygen reduction reaction (ORR).

2.2 Oxygen Vacancies and Catalytic Activity

The concentration and mobility of the vacancies in oxygen are also important parameters that influence the catalytic activities of perovskites. Large amounts of vacancy in compounds such as $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) as well as $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.0}\text{O}_3$ (BSCF) enhance oxygen adsorption, dissociation, and diffusion- a key process in the ORR (Jiang et al.2019 as well as Li et al.2021). Perovskites have highly tunable catalysts because they have been utilized to fine-tune the dependence on defect chemistry or doping.

2.3 Proton Conductivity

Due to their ability to fit in protons by hydration of oxygen gaps, certain perovskites, especially BaCeO_3 and BaZrO_3 ones, can be highly protonically conducted within moisture conditions. This property makes them attractive alternatives to the electrolytes of PCFCs at the intermediate temperatures (Kreuer et al.,2003). BaZrO_3 offers low conductivity with greater chemical stability and BaCeO_3 unsustainable in atmospheres with CO_2 . In order to trade off conductivity and stability, Y^{3+} or Gd^{3+} , doped solids (i.e., $\text{BaCe}_{1-x}\text{Zr}_x\text{O}_3$) have been explored (Rehman et al. 2023).

3. Perovskites as Electrodes in Fuel Cells

Electrode material results have a profound influence on the stability and electrochemical activity of the material, which affects fuel cell performance and life. Perovskite oxides are particularly impressive cathodes and anodes due to their catalytic properties, structural flexibility and mixed ionic-electronic conductivity (MIEC). They perform better than conventional electrode materials in most fuel cell configurations because of their ability to withstand the oxygen vacancy and undergo redox activation (Steele et al., 2001 and Li et al., 2021).

Table — Perovskite Materials as Electrodes in Fuel Cells

Electrode type	Perovskite compositions (examples)	Function role /	Advantages	Key performance indicators	Representative references
SOFC Cathodes (MIEC)	$\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (LSCF), $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.0}\text{O}_3$ (BSCF)	Oxygen reduction reaction (ORR)	High mixed ionic-electronic conductivity (MIEC), fast ORR kinetics, good performance at intermediate T (600–800 °C)	Area specific resistance (ASR), oxygen surface exchange coefficient, TEC compatibility	Zhao et al.2022 as well as Shi et al.2020
Low-Co / Co-free Cathodes	Fe-based double perovskites ($\text{Sr}_2\text{FeMoO}_6$, $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$), $\text{PrBaCo}_2\text{O}_{5+\delta}$	ORR at intermediate –low T	Reduced Co content → lower cost, improved chemical stability	ORR activity, durability under $\text{CO}_2/\text{H}_2\text{O}$ exposure	Kasyanova et al.2022 as well as Giddey et al.2013
SOFC Anodes	$\text{Sr}_2\text{FeMoO}_6$, $\text{La}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$, Sr-doped ferrites	Fuel oxidation reaction	Tolerant to sulfur & coking, direct hydrocarbon operation possible	Electronic conductivity, redox stability, fuel utilization efficiency	Wang et al.2011 as well as Skutina et al.2021

Electrode type	Perovskite compositions (examples)	Function / role	Advantages	Key performance indicators	Representative references
Exsolution-based Electrodes	Ni/Co-doped perovskites (e.g., $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$)	Self-generation of embedded nanoparticles	High catalytic activity, anchored nanoparticles prevent agglomeration → long-term stability	Exsolved nanoparticle distribution, cycling stability	Kim et al.2024 as well as Zhang et al.2022
PCFC Electrodes (Triple Conductors)	$\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_{3-\delta}$ -based composites with perovskites	Proton, oxide-ion & electron conduction	Enhanced electrode kinetics due to triple conductivity	Proton conductivity, electrode polarization resistance, stability in $\text{CO}_2/\text{H}_2\text{O}$	Ding et al.2020 as well as Ni et al.2018
RSOFC Oxygen Electrodes	LSCF, BSCF, and their doped variants	Operate in both SOFC (ORR) & SOEC (OER) modes	Bifunctional activity, tunable oxygen vacancies	Symmetric polarization resistance, redox cycling stability	Zhang et al.2021 as well as Shao et al.2016

3.1 Perovskite Cathodes

The overall performance of SOFCs is limited by a thermodynamically sluggish catalyzed reactions (oxygen reductions reaction) at the cathode. The popular conventional cathodes such as $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM), have low ionic conductivity and high stability that makes them less useful at intermediate temperatures (500 -800 °C) (Skinner et al., 2001).

Due to its higher ORR activity as well as the situation and spreading conductivity, perovskites with higher oxygen vacancy concentration -such as $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$ -(LSCF) as well as $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.3}\text{O}_3$ -(BSCF) become the most promising energy source (Jiang et al., 2019). These substances facilitate faster diffusion, dissociation and adsorption of oxygen. Nevertheless, problems such as the incapacity to separate strontium on the cathode surface may deteriorate performance (Porotnikova et al.2024).

Some more recent means of circumventing them include:

- Intrusion of nanoparticles and coating the surface to prevent segregation of Sr (Li et al., 2020).
- Heterostructured cathodes, enhancing the diffusion of oxygen by mixing perovskites in ionic conductors (like Sm-doped CeO_2) (Bai et al., 2024).
- Nanostructuring and thin-film engineering, which can be used to augment the ORR and improve the active surface area (Acosta et al., 2019).

3.2 Perovskite Anodes

Traditionally used SOFC anodes like Ni-YSZ (yttria-stabilized zirconia) do not perform well in regards to redox stability, carbon deposition and sulfur poisoning when using them as fuels (Minh et al., 2004). They are however very electrically conductive. Due to their resistance to coking and their redox properties that can be switched, perovskite-based anode materials are currently under investigation as potential alternatives.

Among the outstanding ones are:

- $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_3$ STFO: This high-incorporation redox-stable electronic conductor demonstrates excellent electrolyte conductivity at reducing environments.
- $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (LSCM) is a solid choice as highly sulfur-selective direct hydrocarbon SOFC, and tolerant of hydrocarbon fuels, and has the ability (Fu et al., 2022).
- Revamped oxygen ion mobility and strong catalytic activity of double perovskites, such as $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_6$ (Du et al.2018).

Recent study contain also confirmed the establishment of composite anodes making use of perovskites with ionic conductors (e.g. Gd-doped ceria or YSZ) to form long triple-phase boundaries (TPBs), which can GIN gain significant electrochemical advantages (Senthil et al., 2021).

4. Perovskites as Electrolytes in Fuel Cells

Given that conversion of electrical energy to chemical energy and vice versa is necessary, electrolytes are indispensable parts of fuel cells since they carry ions but hinder electrical conductivity. Electrolytes of high-performance fuel cells need high ionic conductivity, chemical stability, and high compatibility with electrodes under operating conditions. Perovskite oxides (especially proton-conducting and oxygen-conducting ion channels) have attracted significant attention as both alternative electrolytes to SOFCs as well as PCFCs (Steele et al.2001 as well as Li et al.2021).

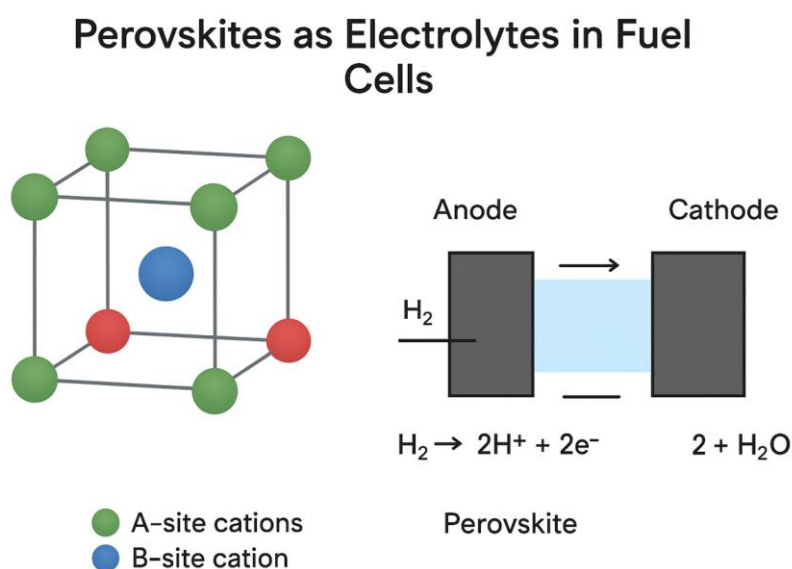


Figure 2. Perovskites as Electrolytes in Fuel Cells.

4.1 Oxygen-Ion Conducting Perovskites

High operating temperatures (800–1000 C) are necessary for adequate oxygen ion conductivity in conventional SOFC electrolytes, including yttria-stabilized zirconia (YSZ). New subsidiary oxides have been studied using LaGaO₃ based oxides and other perovskite based electrolytes as a means of reducing operating temperature.

- LSGM: Doping LaGaO₃ with Sr and Mg increases the ionic conductivity and oxygen vacancy concentration by more than YSZ and by around 0.14 S cm⁻¹ at 800 C (Ishihara et al., 1994 as well as Tao et al., 2007).
- Capturesobs block type: of intermediate-temperature SOFCs (IT-SOFCs) ULSGM would be suited because of the low activation energy and oxygen ion diffusions.

4.2 Proton-Conducting Perovskites

Proton-conducting perovskites have become suitable as the fuel cell electrolyte at temperatures of between 400 to 700 C due to the offering of better long durability and reduction in thermal stress.

BaCeO₃-based perovskites (BCY) are trivalent cation doped by trivalent cations such as Y³⁺, Gd³⁺, and Sm³⁺ and show high proton conductivity (>10⁻² S cm⁻¹ at 600 °C) (Kreuer et al., 2003). BCY, in contrast, is unstable chemically and forms hydroxides or BaCO₃ in CO₂ atmospheres and H₂O atmospheres.

- The BZY-based perovskites: barium-zirconium-yttrium based perovskites are characterized by high level of chemical stability along with slack proton conductivity due to high proton velocity (Katahira et al., 2000).
- One of the most promising alternatives to solid solutions of $Ce_{1-x}Zr_xO_3$ is Y-doped $BaCe_{0.7}Zr_{0.2}Y_{0.1}O_3$ (BCZY). The addition of Ce and Zr leads to higher conductivity and stability (Rehman et al., 2024).

5. Challenges and Limitations of Perovskite-Based Fuel Cells

Perovskite oxides are promising as fuel cell electrode and electrolyte materials, however, many scientific, engineering and marketing challenges remain. These disadvantages make their use not so widely spread as compared to the traditional NiCZ-based systems.

5.1 Chemical and Structural Instability

A wide range of perovskite oxides, particularly those doped with Sr and Ba, degrade chemically in atmospheres with high CO_2 and high H_2O concentrations. As an example, when using the electrolyte in a humidified/ CO_2 rich environment, some formation of $BaCO_3$ and hydroxides is present in the $BaCeO_3$ -based electrolyte, one of the factors that leads to structural collapses and loss of conductivity (Kreuer et al., 2003 and Rehman et al., 2024). On the same note, insulating SrO phases Classification with deactivate oxygen reduction side (ORR) sites are produced when Sr is segregated by cathode material, e.g. LSCF and BSCF (Porotnikova et al., 2024).

5.2 Thermal and Mechanical Compatibility

The difference in thermal expansion coefficients (TECs) between perovskite electrodes and electrolytes and more popular electrolytes like YSZ or GDC is a major problem in the development of perovskite-based fuel cell designs. This can lead to microcracking, interfacial delamination, as well as a gradual decrease in stability when thermal cycling is applied (Bai et al., 2024). Also, at redox conditions, part of perovskites undergo a redistribution of oxygen vacancies that varies lattice parameters and augments stress loads (Li et al., 2020).

5.3 Limited Long-Term Durability

Perovskite electrodes bought in bulk and used over the long run may also result in phase segregation, cationic migration and grain coarsening. Such events undermine the activity of electrodes and reduce ionic/electronic conductivity (Jiang et al., 2019). The movement of Co and Fe cation, e.g. has been related to prolonged utilization of LSCF cathodes leading to microstructural instability (Adlers et al., 2004).

5.4 Processing and Fabrication Challenges

Complex synthesis techniques (solid-state reaction, sol-gel, as well as pulsed laser deposition), higher sintering temperatures, and exact stoichiometry control are frequently needed to manufacture perovskite-based electrolyte and electrode (Steele et al., 2001). Due to its refractory characteristic, $BaZrO_3$ -based proton conductor is extremely difficult to sinter and requires expensive sintering aids (Katahira et al., 2000). These issues increase the cost of producing, and obscure scaling, in comparison with Ni-YSZ systems.

5.5 Intermediate-Temperature Operation Limitations

Perovskites are attractive in SOFCs with intermediate temperatures (500 -700 C), but they can be challenging to retain high conductivity and stability at such temperatures. Whereas $BaCeO_3$ -based electrolytes support high conductivity and low durability, $BaZrO_3$ -based electrolytes are stable and mixed with limited conductivity (Li et al., 2021). The optimal balance is also among the highest priorities of research.

5.6 Fuel Flexibility and Redox Cycling Issues

Although some self-anions of perovskites (e.g., LSCM and $SrTi_{1-x}Fe_xO_3$) already show the capacity to oxidize hydrocarbons, there are other issues, such as redox instability, carbon deposition and sulfur poisoning (Goodenough et al., 2007). Redox cycling and repetitive shortage of fuel may result in damage to the structural

level, which is impossible to fix.

6. Future Perspectives

Amid protonic ceramic fuel cells (PCFCs) and intermediate-temperature SOFCs, perovskite-based fuel cells (PFCs) are rapidly steering towards the durability and reduction in operating temperature (around 400-600 °C). The development of highly conductive protonic perovskite electrolytes as well as triple-ionic/electronic conductor (TIEC) cathodes suggests that stability-versus-power-density trade-offs that persist into the current

era can be reduced through careful A/B-site chemistry and defect/strain engineering (Zhang et al., 2024).

6.1 Materials discovery will prioritize Sr- and Co-lean perovskites, double-perovskite frameworks, and high-entropy oxide design.

Through high-throughput computation and machine learning, the direction is changing to Fe-rich double perovskites in addition to entropy-stabilized electrolytes (such as HEO Ba-cerate / zirconate solid solutions) to reduce segregation of cations, scarcity of elements / toxicity. The designs reduce the critical-metal levels and offer variable transport and increased stability limits (Zheng et al., 2024).

6.2 Controlling surface chemistry is now central to lifetime gains.

Reduction in chromium toxicity and A-site (Sr) segregation continue to require enhancement of the long-term operation of perovskite cathodes. Since surface phases are strongly linked to oxygen exchange kinetics, because the former depends on the latter, surface reconstruction, dopant, and atomic-scale surface-termination studies are becoming techniques enabling the emerging technologies, head of which are surface terminations. It is expected that the application of operando toolkits and standardized stress test will be expanded to guide the design of surfaces without surfactants (Samreen et al., 2023).

6.3 Exsolution-enabled nanocatalysis will mature from concept to process.

Perovskite matrices with in-situ dissolve socketed metal and alloy nanoparticle (Ni, Co, Fe, and Ru), are also providing electrodes with commercially-available triple-phase boundaries resistant to coke and sulfur. The next stage in restoring performance after redox abuse can be performed by the use of regeneration cycles, multi-element exsolved alloys, and spatially patterned exsolution, which is electrically or chemically induced. Coupling exsolution and 1D/2D designs (nanofibers, porous scaffolds) do not need to reduce the density of active sites, and so might be further enhanced (Xie et al., 2024).

6.4 Electrolyte breakthroughs aim at thinner, denser, more CO₂-resistant films.

Our short-term target is the scalable thin film production (inkjet/spin/PLD/ALD) of sub-micron density and low ohmic losses; the BZCYYb-based proton conductor already exhibit high conduction at <600C. In parallel, recently found mixed OH⁻/H⁺ ceramic conductors provide a proving avenue to achievable even lower-temperature operation, however, there remains the need to establish how compatible they are with traditional electrode chemistries. Finally, Zr-based chemistries and protective surface coats are also useful countermeasures to the CO₂ reaction (carbonate formation) with Ba-rich perovskites, which is, however, a design drawback (Guo et al., 2022).

6.5 Manufacturing will be re-imagined around digital printing and additive routes.

High density Inkjet, aerosol and direct-ink-writing (DIW) techniques are being used to construct dense electrolytes, as well as architected electrodes with glaringly low region-specific resistances and impressive adhesion This is now also being applied to produce tubular or planar large-area cells in 3D printing and using commodity powders This is now being moved out of the laboratory, into pilot-scale, using tubular or planar large-area cells. Closed-loop control printing processes, in-line metrology especially, are also expected to become

prevalent in the next three to five years (Zou et al., 2024).

6.6 System-level integration will emphasize reversibility and fuel flexibility.

Reversible SOCs (Rsocs) which employ perovskite electrodes will be made using the same material advancements, where light hydrocarbons or ammonia can be used in the intermediate temperature or they can be directly used at lower temperatures, and they can store or release them at high temperatures. Splits rings Both the SOFC and SOEC modes will require co-optimisation of the position of anode as well as cathode chemistries and supports in arrange on the way to meet the high-current density goal with minimal decrease in the degradation groups (Meisel et al., 2025).

7. Conclusion

Perovskite based materials are some of the most appealing materials to develop in fuels cell technologies due to their high activity in catalysis, dual ionic and electronic conductivity, structural manipulation and the ability to operate in intermediate temperatures. Although LaGaO₃-based and also BaCeO₃/BaZrO₃-based oxide are used as substitutes of traditional YSZ in reducing overall temperature, perovskite type such LSCF, BSCF and LSCM also show excellent oxygen reduction and also reduce hydrocarbons oxidation as electrodes. The ability to substitute with some kind of substitutes in the A- and B-sites makes it possible to have customized characteristics to certain electrochemical functions. Nevertheless, despite these advantages, the number of challenges and limitations is quite significant. The challenges in the large-scale commercialization include surface degradation (Sr segregation), instability under CO₂ /H₂O conditions, low long-term stability, and difficulties in fabrication. Namely, BaZrO₃-based solutions possess smaller yet better resilience conductivity in comparison to products based on BaCeO₃ that have high proton conductivity but are frail. Further besides, cost competitiveness in comparison to Ni cell based on YSZ remains a problem, interfaces and front end incompatibilities and processing constraints.

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