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Chemistry Europe
European Chemical Societies Publishing

REVIEW OPEN ACCESS

NiO Dissolution in Molten Carbonate Fuel Cell Cathodes: Challenges and Strategies for Long-Term Stability

Kosar Hasanpoursorkhdehi | Michele Maragliano | Dario Bove | Barbara Bosio

Department of Civil, Chemical and Environmental Engineering (DICCA), University of Genoa, Genoa, Italy

Correspondence: Dario Bove (dario.bove@unige.it)

Received: 10 March 2026 | **Revised:** 31 May 2026 | **Accepted:** 4 June 2026

Keywords: fuel cell | molten carbonate fuel cell | NiO dissolution

ABSTRACT

Molten carbonate fuel cells (MCFCs) are highly promising for efficient electricity generation and selective CO_2 capture, particularly in hard-to-abate sectors such as maritime and heavy industry. However, their operational lifetime is constrained by the dissolution of nickel oxide (NiO) cathodes in molten carbonate electrolytes, which leads to voltage degradation and potential short-circuiting. This review evaluates strategies to enhance cathode stability and reduce NiO solubility. Key approaches include advanced coatings ($LiCoO_2$, TiO_2, ZrO_2, and Co_3O_4), doping, partial replacement with alternative materials ($LiFeO_2$, La-based oxides, and bismuth–yttrium–samarium oxide [BYS]), and electrolyte modification using alkaline and rare-earth oxides. Various fabrication techniques, including sol–gel, Pechini, atomic layer deposition (ALD), tape-casting, and slurry infiltration, were applied to produce uniform, adherent, and chemically stable cathode layers. Reported studies show that optimized coatings and dopants can reduce NiO dissolution by 50%–60%, enhance electronic conductivity, and improve structural stability under prolonged operation. Multilayer cathode architectures and modified electrolytes further improve oxygen reduction kinetics, mechanical robustness, and power density. Collectively, these strategies significantly extend MCFC lifetime and performance, offering a pathway toward cost-effective, durable, and high-performance cells. The findings underscore the critical role of integrating material innovations and electrolyte engineering to advance MCFC commercialization while simultaneously supporting CO_2 mitigation.

1 | Introduction

Molten carbonate fuel cells (MCFCs) serve as both sustainable power generators and CO_2-selective concentrators for carbon capture. Their ability to separate and concentrate CO_2 makes them ideal for hard-to-abate sectors like maritime and heavy industry [1, 2]. With strict environmental regulations pushing for lower emissions, MCFCs offer an efficient solution to meet these targets [3]. They maintain high energy efficiency while reducing CO_2 emissions. Their seamless integration into existing industrial processes enhances their viability as a near-term carbon mitigation technology [4]. MCFCs operate at temperatures between 600°C and 700°C and use molten carbonate electrolytes composed mainly of lithium, potassium, and sodium carbonates [5]. As shown in Figure 1, they are contained within a ceramic matrix made of $LiAlO_2$, positioned between the anode and cathode. Carbonate ions are transferred from the cathode to the anode according to the following reactions (1–3): At the anode, hydrogen (H_2) reacts with the carbonate ions (CO_3^{2-}) to produce water (H_2O), carbon dioxide (CO_2), and ions. At the cathode, oxygen (O_2) combines with CO_2 and ions, resulting in the formation of carbonate ions (CO_3^{2-}) [6].

Anodic reaction

$$H_2 + CO_3^{2-} \rightarrow CO_2 + 2e^- + H_2O \quad (1)$$

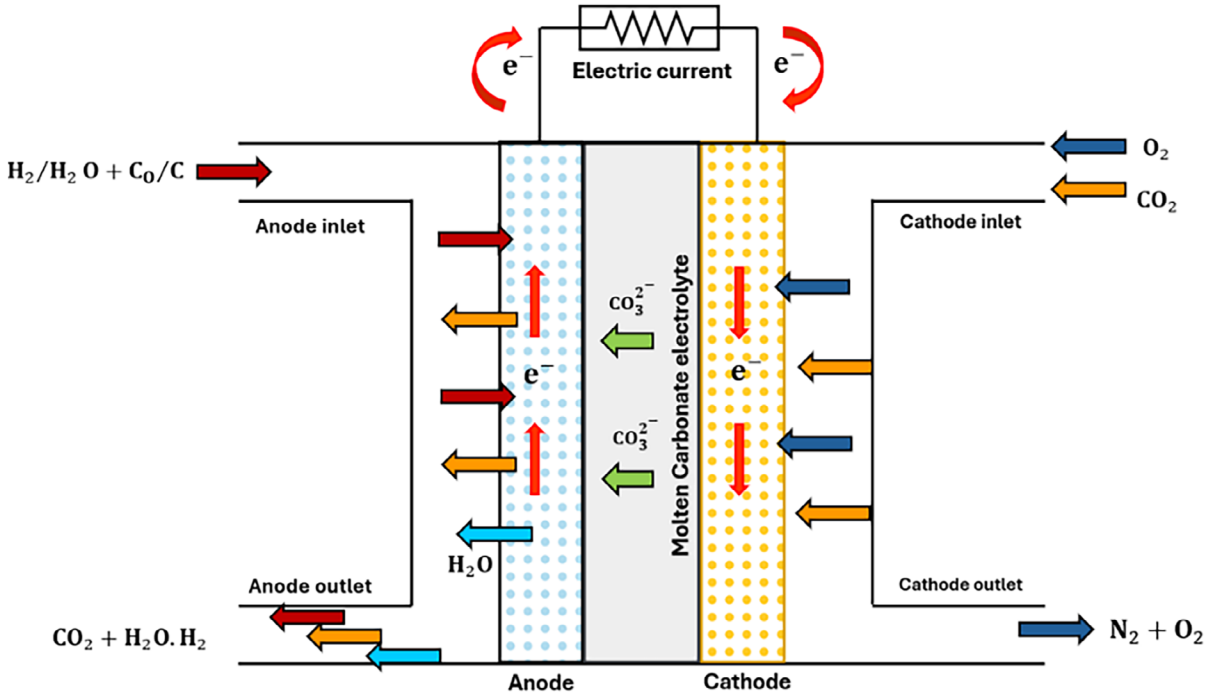

FIGURE 1 | Schematic diagram of MCFC.

Cathodic reaction

$$\frac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-} \quad (2)$$

Overall reaction

$$H_2 + \frac{1}{2}O_2 + CO_2 \rightarrow H_2O + CO_2 \quad (3)$$

Carbon capture can be achieved through various methods, such as amine absorption, calcium hydroxide, and MCFCs [7, 8]. As previously highlighted, MCFCs stand out as an advanced technique that not only captures CO_2 but also generates electricity efficiently. Recent developments focus on enhancing electrode materials and optimizing operating conditions to improve performance [6, 9].

In this context, recent reviews on MCFC electrode reactions have emphasized that cathode/electrolyte interfacial phenomena, electrolyte stability, and Ni-based cathode degradation are among the major factors limiting long-term MCFC operation [10].

MCFCs offer high efficiency and fuel flexibility, making them suitable for industrial applications. However, the process remains expensive, limiting widespread adoption. Our goal is to extend the lifetime of MCFCs, ensuring their long-term viability and cost-effectiveness in carbon capture and clean energy production [11–13].

Extending the lifespan of MCFCs is a critical objective for their commercialization, with a target operational lifetime of 40,000 h and a voltage decay rate of less than 10% over this period [14, 15]. A major focus in the development of electrode materials for MCFCs is improving their chemical and physicochemical stability to enhance durability. The voltage degradation in MCFCs typically occurs in two distinct phases, as illustrated in Figure 2. The initial phase is characterized by a gradual voltage decline,

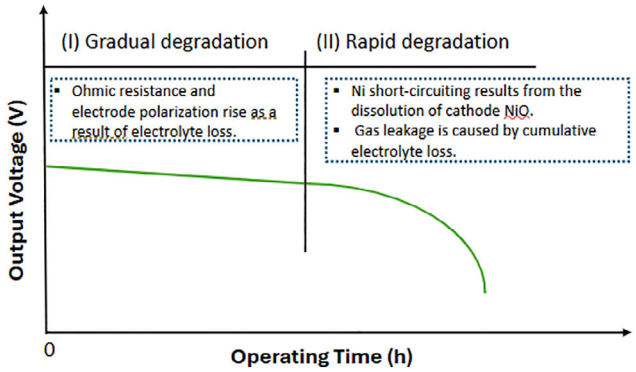

FIGURE 2 | Schematic representation of MCFC degradation over operating time (under constant current conditions).

mainly associated with increasing internal resistance and electrode polarization resulting from carbonate electrolyte loss. This is followed by a second phase of rapid degradation, typically linked to nickel short-circuiting or gas cross-leakage [16].

Numerous studies identify short-circuiting caused by metallic nickel precipitation from the cathode as the dominant failure mechanism in MCFCs [17]. Nickel oxide (NiO) is widely employed as the cathode material due to its stability under oxidative conditions, high electrochemical conductivity, and suitable porosity for gas diffusion [18]. However, a major limitation of NiO cathodes is their dissolution in molten carbonate, which critically affects the operational lifetime of MCFCs [19, 20].

Early systematic investigations demonstrated that the stability of NiO cathodes in molten carbonate environments is intrinsically linked to the thermodynamic acid–base behavior of the electrolyte and to the partial pressure of CO_2 at the cathode. In

particular, the dissolution of NiO was shown to proceed through carbonate-mediated mechanisms that strongly depend on operating temperature, electrolyte composition, and gas atmosphere, ultimately leading to nickel migration and internal short-circuiting phenomena [21, 22].

Although the solubility of NiO in the carbonate electrolyte at the cathode is relatively low (approximately 10–15 ppm), its dissolution rate is significant and strongly influenced by the CO_2 partial pressure and lithium content [5, 16]. Under typical MCFC operating conditions, NiO dissolution proceeds predominantly via the so-called acidic mechanism [6, 23], as described below.

$$NiO \rightarrow Ni^{2+} + O^{2-} \tag{4}$$

$$CO_2 + O^{2-} \rightarrow CO_3^{2-} \tag{5}$$

The complete dissolution reaction is as follows:

$$NiO + CO_2 = Ni^{2+} + CO_3^{2-} \tag{6}$$

This phenomenon is governed by the acid–base equilibrium of the molten carbonate electrolyte. Under high CO_2 partial pressure, the activity of oxide ions in the melt decreases, making the electrolyte effectively more acidic and promoting the formation of soluble nickel species from solid NiO [19, 22–24]. Although the NiO solubility is relatively low, typically on the order of 10–15 ppm, even limited dissolution can become critical during long-term operation [19, 20]. Dissolved nickel species can migrate through the electrolyte-filled matrix toward regions with lower oxygen potential, where they may be reduced and precipitate as metallic nickel. Progressive nickel deposition can form electronically conductive paths across the electrolyte matrix, leading to internal short-circuiting and accelerated voltage degradation [15–18]. This mechanism is particularly important under CO_2-rich or pressurized MCFC operation, where elevated CO_2 partial pressure increases the driving force for acidic NiO dissolution [19, 20, 24].

Its role becomes even more relevant when MCFCs are considered not only as power generators but also as electrochemical CO_2 separators for industrial carbon-capture applications. Recent studies have investigated MCFC integration in maritime systems, steel production, biomass-based power plants, and optimized CO_2 capture configurations, highlighting the growing interest in operating MCFCs under CO_2-rich and process-integrated conditions [7, 11–13, 25–28]. In these applications, the cathode may experience variable CO_2 partial pressure, flue gas impurities, pressurized operation, electrolyte redistribution, and repeated thermal transients, all of which can alter the carbonate acid–base equilibrium and promote NiO dissolution.

From a commercial perspective, the dissolution–migration–reduction mechanism represents one of the main degradation pathways limiting long-term MCFC operation and scale-up. Accelerated nickel dissolution and redeposition contribute to increased internal resistance, performance decay, and reduced stack lifetime, posing major challenges for cost-effective and durable MCFC deployment [25–30].

Although cobalt-containing coatings and doped cathode materials can effectively suppress NiO dissolution, their large-scale implementation is limited by cost and material availability, motivating the development of scalable and cobalt-lean stabilization strategies.

This review critically examines the main approaches proposed to mitigate NiO dissolution and short-circuiting in MCFCs. The selected literature includes peer-reviewed experimental and modeling studies on NiO solubility, nickel precipitation, cathode degradation, voltage decay, electrolyte modification, cathode microstructure, and long-term MCFC operation. Recent investigations on cathode architecture, matrix degradation, electrolyte management, flue-gas operation, maritime applications, and techno-economic assessment are also discussed to evaluate the practical relevance of each stabilization strategy under realistic operating conditions.

Three main mitigation approaches are analyzed:

1. Advanced cathode coatings and doping strategies to improve stability and reduce degradation;
2. Alternative cathode materials with lower solubility and higher chemical stability than NiO;
3. Modification of NiO and electrolyte chemistry to suppress dissolution and nickel redeposition.

Compared with previous reviews focused more broadly on MCFC materials or degradation phenomena, the present work specifically addresses NiO dissolution as a coupled cathode–electrolyte–operating-condition problem. Its novelty lies not only in summarizing individual stabilization strategies but also in comparing coatings, doped NiO, alternative cathodes, multilayer or core–shell architectures, and electrolyte modification within a unified degradation framework.

2 | Strategies to Limit NiO Dissolution in MCFCs

2.1 | Enhanced NiO Cathodes with Doping and Coatings

Among the earliest Stabilization strategies, lithiated cobalt-based coatings were shown to significantly suppress NiO dissolution by strengthening metal–oxygen bonding and limiting direct contact between NiO and the molten carbonate electrolyte. These findings established $LiCoO_2$-based surface modification as a reference approach for improving MCFC cathode durability [31, 32].

2.1.1 | $LiCoO_2$ Is Employed as a Cathode Coating

Surface modification of NiO cathodes through doping or coatings is among the most effective strategies to mitigate corrosion and NiO dissolution in MCFCs.

$LiCoO_2$ has attracted particular attention due to its superior electrical conductivity and chemical stability compared to $LiFeO_2$, making it a preferred material for protective coatings [33–36].

A wide range of deposition techniques has been explored, including sol–gel [36–38], Pechini [39], solution impregnation [40, 41],

electroplating [41], electroless deposition [42, 43], galvanostatic and chemical deposition [43–45], microencapsulation [46], as well as mechanical and atomic layer deposition (ALD) [47–51]. These approaches aim to form uniform and adherent layers that can lower NiO solubility by up to 60% [35, 36, 40, 43, 52].

Han et al. [40] demonstrated that $LiCoO_2$-coated NiO cathodes (≥0.2 mol %) maintained stable Ni content under operating pressures of 1–5 atm, confirming that Co strengthens Ni—O bonding and reduces NiO dissolution through a chemical mechanism. Similarly, Goo Kim et al. [41] observed a 56% decrease in Ni precipitation after 1000 h with sol-impregnated $LiCoO_2$ coatings, although it was accompanied by a slight initial voltage drop.

Other studies corroborate these results. Improved long-term stability of sol–gel-derived $LiCoO_2$-coated Ni cathodes was reported by Paoletti et al. [53] and Brenscheidt et al. [54], but both studies also showed that coating thickness and porosity significantly impact polarization resistance. Brenscheidt et al. [54] measured that a $LiCoO_2$ coating of about 140 µm reduced the nickel transfer rate by about a factor of two. According to lifetime modeling, $LiCoO_2$ coatings with thicknesses of around 95 µm would be needed to achieve an operating lifespan of about 40,000 h. It was anticipated that such thick coatings would substantially increase cell resistance, thereby raising polarization losses and impairing electrochemical performance overall. These results highlight the intrinsic trade-off between resistive losses arising from transport and from cathode stabilization.

Lee et al. [52] deposited a nano-Co_3O_4 layer via the Pechini method, leading to the formation of a stable $LiCo_{1-\gamma}Ni_\gamma O_2$ phase that improved voltage and reduced NiO solubility over 300 h of operation.

More recently, Kim et al. [55] applied nanosized $LiCoO_2$ coatings by tape casting and hot pressing, highlighting the critical role of thickness optimization. Insufficient coating failed to expand triple-phase boundaries (TPBs), whereas excessive thickness hindered gas diffusion. Optimal performance was obtained with 15–20 wt% coatings, which ensured stable operation over time.

Mustafa et al. [56] further developed Co-doped lithiated NiO via a low-cost, water-based synthesis. Doping increased electrical conductivity from 3.63 to 12.16 S cm^{-1}, while scanning electron microscopy (SEM) analysis revealed spherical particles with homogeneous cobalt-rich distribution, favorable for cathode stability Figure 3 Overall, these studies demonstrate that $LiCoO_2$ coatings and Co doping significantly enhance NiO cathode durability. Nevertheless, optimization of morphology and deposition parameters remains essential to minimize polarization losses and ensure long-term MCFC performance.

2.1.2 | Atomic Layer Deposition (ALD)

ALD enables the fabrication of conformal, dense, and nanometric oxide coatings, overcoming the adhesion, uniformity, and thickness-control limitations of conventional methods (e.g., sol–gel, electrodeposition, and sputtering) [47, 48]. TiO_2 layers on porous Ni cathodes reduced Ni solubility by 50% after 230 h in Li_2CO_3/K_2CO_3 (62:38 mol%) at 650°C while forming interfacial LixTyNiO phases that influenced the in situ electrochemical response Figure 4. Comparative studies [48] showed that CeO_2 coatings also halved Ni solubility while preserving structure, whereas Co_3O_4 provided low resistance but failed to sustain the

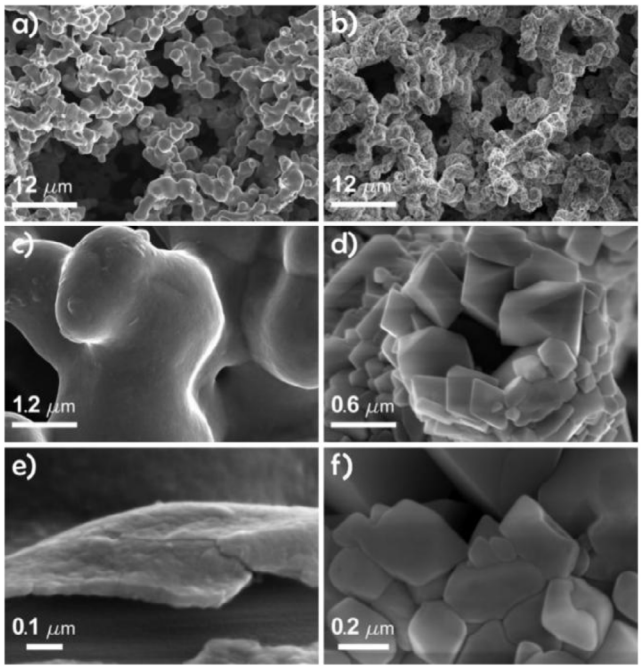

FIGURE 4 | SEM images of a porous Ni electrode coated with a 300 nm TiO_2 layer deposited by ALD, recorded before exposure (a,c,e) and after 230 h of immersion in molten Li_2CO_3–K_2CO_3 (62:38 mol%) at 650°C (b,d,f). Reproduced from Ref. [48]. Copyright (2013) with permission from Elsevier.

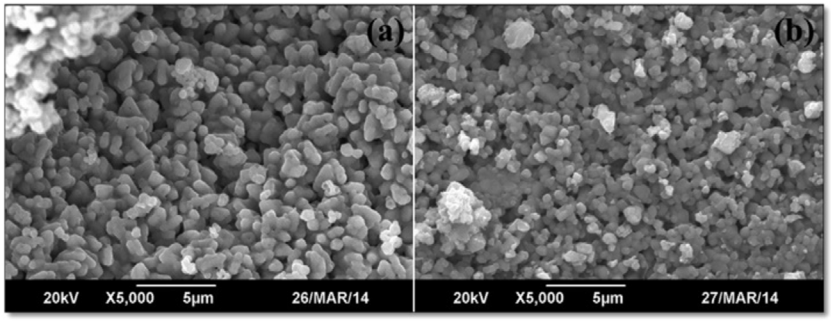

FIGURE 3 | SEM images of (a) $Li_{0.68}Ni_{1.32}O_2$ and (b) $LiNi_{0.8}Co_{0.2}O_2$. Reproduced from Ref. [56]. Copyright (2015) with permission from Elsevier.

oxygen reduction potential (Figure 5). Among tested oxides, TiO_2 exhibited the most favorable balance between dissolution resistance and oxygen reduction reaction (ORR) activity [49].

Niobium oxide coatings applied by ALD have been suggested as a substitute protective method for MCFC cathodes in more recent times. Porous Ni cathodes were coated with conformal NbO_5 layers of regulated thickness, which were then tested at 650°C in molten Li_2CO_3–K_2CO_3 eutectic. The stabilization period of the open-circuit potential was considerably decreased, and NiO solubility was significantly reduced by a 20 nm NbO_5 coating. The presence of a niobium-induced electrocatalytic effect was suggested by the electrochemical impedance spectroscopy, which showed a brief increase in total and mass-transfer resistances, followed by a sharp decline. The creation of mixed Ni–Nb–Li oxide phases, as revealed by post-test surface studies, highlighted the dual functional significance of Nb_2O_5 coatings by protecting the Ni cathode from dissolving and maintaining its oxygen reduction capability [50].

Kim et al. [51] further demonstrated that ultrathin ZrO_2 coatings uniformly covered the porous cathode surface without altering its morphology. X-ray photoelectron spectroscopy (XPS) analysis confirmed the successful surface modification of the coated cathodes, while transmission electron microscopy (TEM) imaging and energy-dispersive spectroscopy (EDS) mapping further verified the conformal morphology and elemental distribution of the coating. Beyond reducing corrosion, the ZrO_2 layer inhibited NiO sintering and enhanced oxygen reduction by electron donation to NiO, thereby improving both performance and long-term stability (Figure 6). Overall, ALD emerges as a precise and scalable approach for tailoring cathode surfaces, with TiO_2 and ZrO_2 coatings offering the most promising results for durable MCFC operation.

2.1.3 | NiO Coated with Alternative Materials

These studies confirm that tailored coatings significantly enhance both efficiency and durability. The electrochemical performance and durability of MCFC cathodes, including resistance

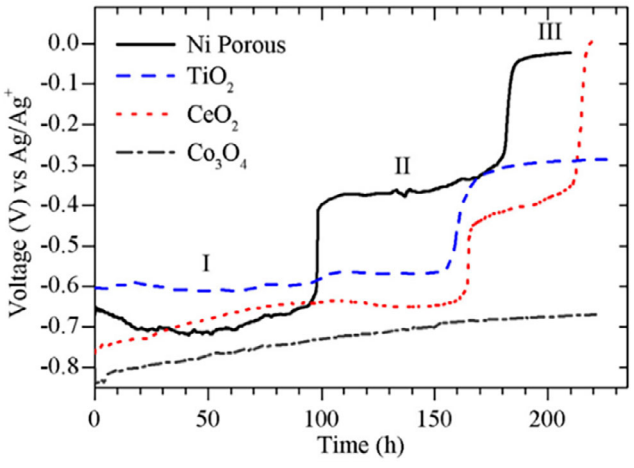

FIGURE 5 | The evolution of the open circuit potential (OCP) during 230 h of immersion in molten Li_2CO_3-K_2CO_3 (62–38 mol%) at 650°C: (a) porous Ni; (b) TiO_2 (50 nm); (c) CeO_2 (27 nm); (d) Co_3O_4 (50 nm). Reproduced from Ref. [49]. Copyright (2014) with permission from Elsevier.

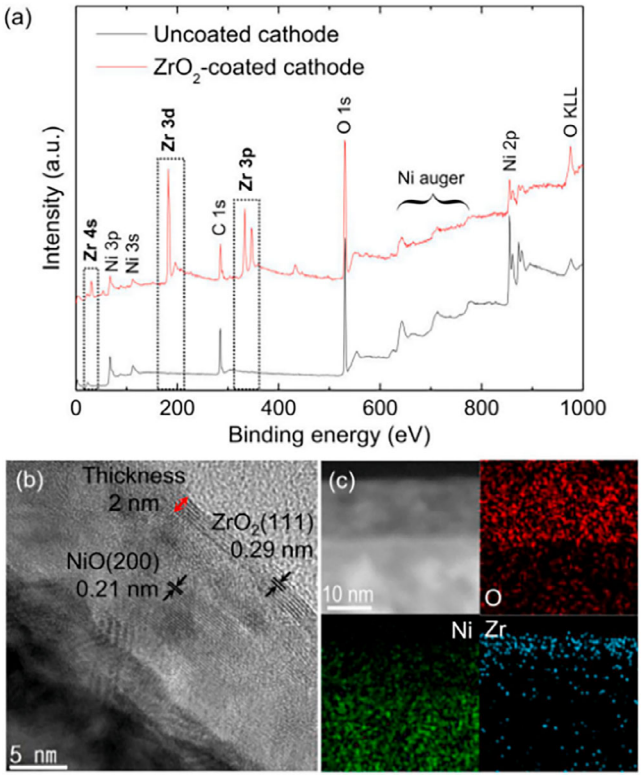

FIGURE 6 | (a) XPS spectra of the uncoated and ZrO_2-coated cathodes; (b) TEM image; and (c) EDS elemental mapping of ZrO_2-coated cathodes. Reproduced from Ref. [51]. Copyright (2021) with permission from Elsevier.

to Ni dissolution, can be enhanced through tailored NiO microstructures and chemical compositions [57–59]. Among the proposed approaches, conductive and corrosion-resistant coatings have proven particularly effective. Silver-based layers, applied either as porous deposits or nanosized sols, enhance electron transport while acting as a protective barrier against NiO corrosion, resulting in reduced ohmic and charge-transfer resistance and stable operation exceeding 1000 h [60–63].

More recently, Komorowska et al. addressed Ni cathode dissolution in MCFCs using a TiO_2/Ag nanocomposite coating deposited by electrophoretic deposition (EPD). Tests in Li/K carbonate electrolyte at 650°C under an air/CO_2 atmosphere showed that the coated cathode significantly reduced Ni dissolution compared with bare Ni. The improved stability was mainly attributed to TiO_2, while Ag enhanced electrical conductivity. In addition, the modified cathode slightly increased the maximum power density from about 90–100 mW cm^{-2}, demonstrating that TiO_2/Ag coatings can effectively mitigate Ni dissolution without negatively affecting MCFC performance [64].

Perovskite (LSCF) and nano-$LiNiO_2$ coatings further promote oxygen reduction kinetics and increase the active surface area while limiting direct contact between NiO and the molten carbonate electrolyte. When coating thickness is properly optimized, cell voltages above 0.87 V at 600–650°C have been reported without evidence of accelerated degradation [61–63] (Figure 7).

Alternative materials, such as BYS ($Bi_{1.5}Y_{0.3}Sm_{0.3}O_{3-\delta}$), enhance mechanical stability and oxygen transport at lower temperatures

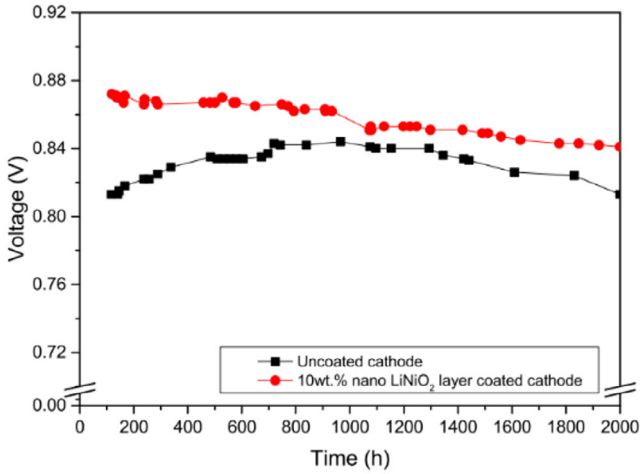

FIGURE 7 | Long-term operational performance of the uncoated cathode cell versus the 10 wt% nano $LiNiO_2$-coated cathode cell. Reproduced from Ref. [63]. Copyright (2019) with permission from Elsevier.

(<600°C), yielding up to 1.84× higher power density at 550°C compared to conventional cathodes [65] (Figure 8). Structural reinforcement strategies, including the use of nickel foam supports and surfactant-controlled infiltration, have also been proposed to improve cathode robustness and microstructural stability [59]. Deposition techniques include sol–gel for thicker films and ALD for precise thin layers; however, corrosion resistance in molten carbonate and overall cost-effectiveness remain key factors for optimization under MCFC conditions.

2.2 | Cathode Material Partial Replacement

Several alternative materials have been investigated as partial or complete replacements for NiO in MCFC cathodes to mitigate nickel dissolution; however, full substitution remains challenging due to trade-offs between chemical stability and electrochemical activity. $LiFeO_2$ exhibits excellent chemical stability and a near-zero dissolution rate, but its limited catalytic activity for

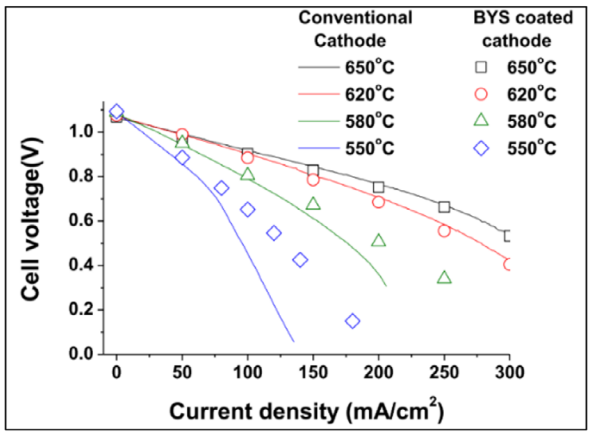

FIGURE 8 | IV curves at various temperatures for a 100 cm^2 single cell utilizing a conventional cathode and a BYS-coated cathode. Reproduced from Ref. [65]. Copyright (2017) with permission from Elsevier.

the ORR restricts its practical applicability. In contrast, $LiCoO_2$ delivers electrochemical performance comparable to NiO while showing an order-of-magnitude lower dissolution rate; when processed in porous form, it also provides sufficient electronic conductivity, making it one of the most promising candidates for partial NiO replacement [38, 39, 66, 67]. Other materials, such as Li_2MnO_3 and $La_{1-x}Sr_xCoO_3$, display low solubility in molten carbonates but suffer from sluggish oxygen reduction kinetics and low exchange current densities, which currently limit their deployment in MCFC cathodes.

Given these intrinsic limitations, partial replacement strategies are often combined with tailored electrode architectures to preserve cathode performance. Wejrzanowski et al. [59] demonstrated that optimized cathode porosity (55%–60%) and multimodal pore size distributions significantly enhance gas and electrolyte transport. Their two-layer cathode design, incorporating nickel foam on the gas side, improved mechanical robustness and power density while compensating for porosity losses associated with NiO oxidation during start-up (Figure 9). Similarly, Ćwieka et al. [58] showed that multilayer cathodes combining porous NiO, nickel foam, and silver improve structural stability and gas diffusion, resulting in superior performance under load compared to conventional NiO cathodes (Figures 10 and 11).

Beyond full or partial material replacement, several studies have focused on chemically modifying NiO to reduce nickel dissolution while preserving electrochemical activity. Choi et al. [66] investigated La- and Ti-modified NiO cathodes, showing that La doping promotes $LaNiO_3$ formation, which enhances electronic conductivity and corrosion resistance. Ti-modified NiO cathodes, when optimized in terms of Ti content and annealing temperature, exhibited improved long-term stability and favorable impedance characteristics. Multicomponent and solid-solution approaches have also been explored. Skibiński et al. [9] further advanced microstructure-driven cathode design by demonstrating that a foam-based layered NiO cathode with controlled pore size distribution achieved significantly higher porosity (68.1%) and a 17% increase in power density compared to conventional single-layer cathodes. The optimized pore architecture reduced mass-transport and charge-transfer resistances while enhancing mechanical robustness. As NiO dissolution is strongly influenced by electrolyte distribution within the porous structure and local CO_2 partial pressure, such architectural optimization may also indirectly contribute to improved long-term cathode stability.

As sustainable substitutes for synthetic polymer-based pore formers, Komorowska et al. [68] examined the use of natural porogens (wheat straw, hemp, and sugar beet pulp) in tape-cast NiO cathodes for MCFC applications. Defect-free cathodes with highly linked pore networks were created using optimized double-porogen systems (starch and post-industrial residues), which achieved low closed porosity (1.0%–1.8%) and open porosity values between 80.5% and 84.8%. With power densities up to 100 mW cm^{-2}, the starch–straw system showed the highest overall fuel cell efficiency among the tested samples. It's interesting to note that the PVB reference sample's highest Darcy permeability did not match its highest power density, suggesting that having too high permeability might not be ideal. As NiO dissolution is

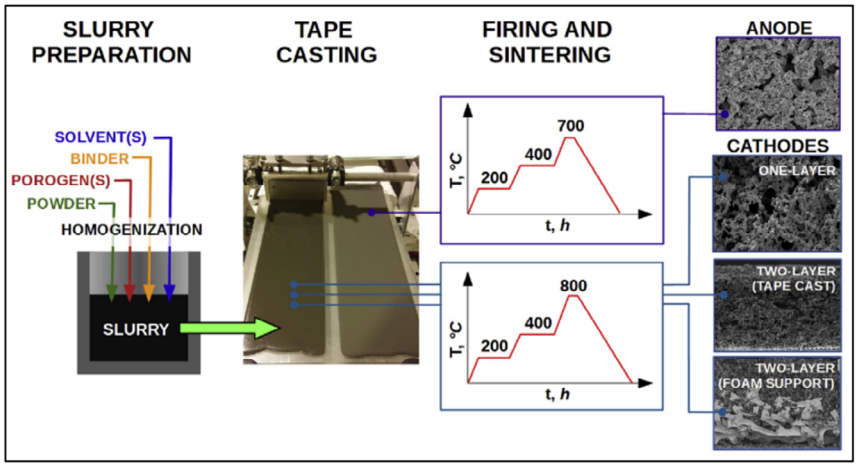

FIGURE 9 | Schematic representation of electrode fabrication by tape casting. Reproduced from Ref. [59]. Copyright (2020) with permission from Elsevier.

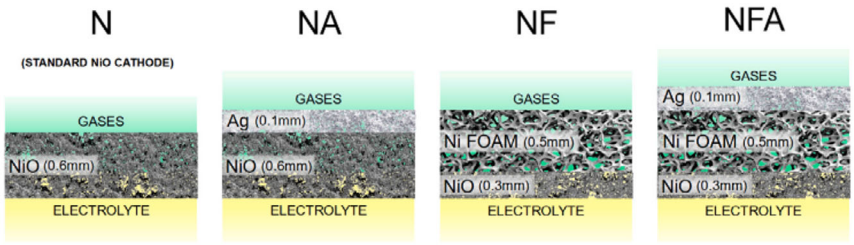

FIGURE 10 | Scheme of microstructure design of analyzed cathodes, their placement within the cell assembly, and the layer thicknesses. Reproduced under terms of the CC-BY license. Ref. [58]. Copyright 2021, The Authors, published by Elsevier.

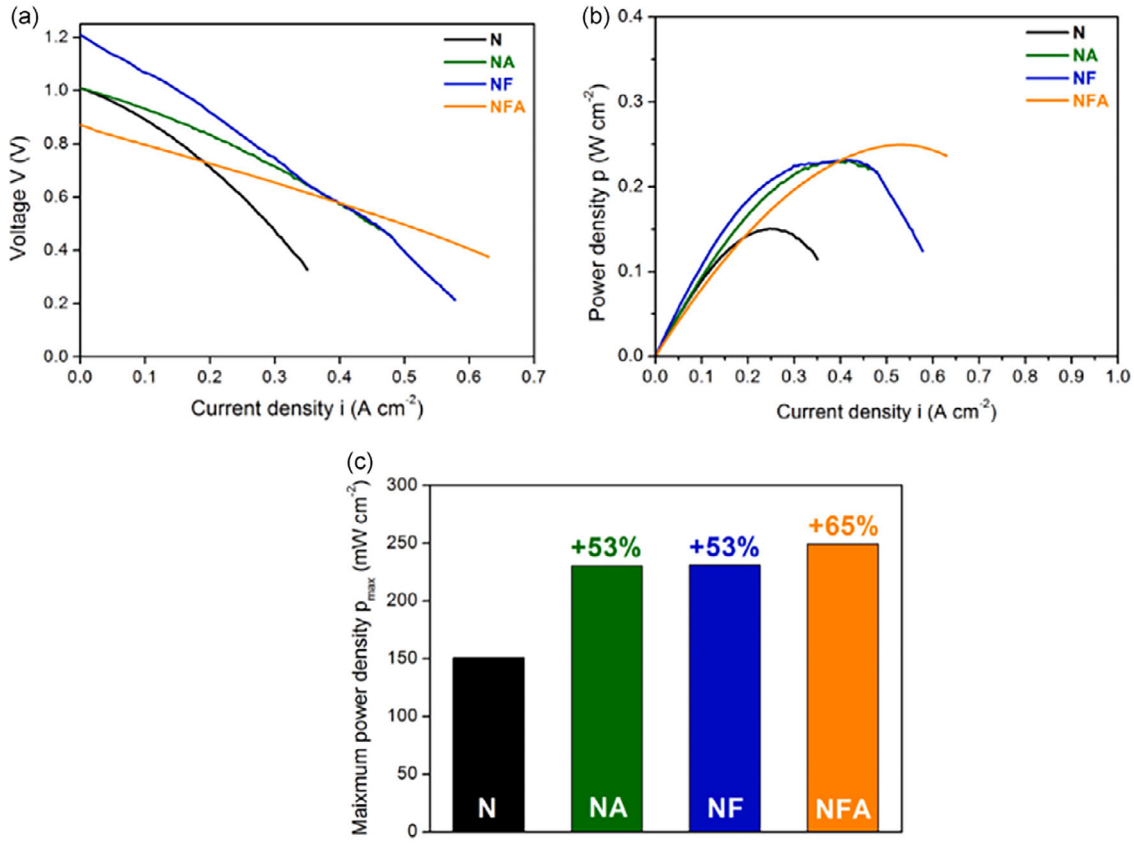

FIGURE 11 | Results from single-cell performance tests of the analyzed cathodes at an operating temperature of 650°C: E-I curves (a), P-I curves (b) and maximum power density (c). Reproduced under terms of the CC-BY license. Ref. [58]. Copyright 2021, The Authors, published by Elsevier.

influenced by electrolyte distribution and local CO_2 partial pressure within the porous structure, such controlled microstructural optimization may also indirectly contribute to improved long-term cathode stability.

Wijayasinghe et al. [67] studied ternary $LiFeO_2$–$LiCoO_2$–NiO compositions synthesized via Pechini and glycine–nitrate routes. While excessive porosity limited the applicability of glycine–nitrate-derived powders, Pechini-derived materials showed adequate phase purity, electronic conductivity, and evidence of solid-solution formation between $LiFeO_2$ and NiO, supporting their use as partially stabilized cathodes.

For hybrid MCFC/SOFC applications, composite cathodes have been proposed to address both chemical stability and mechanical robustness. Komorowska et al. [69] developed Ni–SDC composite cathodes, demonstrating that optimized sintering temperatures (800–1000°C) and controlled reducing atmospheres improve conductivity and mechanical strength. A two-step thermal treatment (oxidizing followed by reducing conditions) was identified as particularly suitable for large-scale cathode fabrication. Among the proposed strategies, engineered core–shell architectures appear especially effective in directly mitigating nickel dissolution. Kim et al. [70] reported a core–shell $Ni_{0.9}Co_{0.1}O$ cathode synthesized via controlled annealing of Ni and Co_3O_4 precursors at 650°C, forming a highly lithiated outer shell. This configuration reduced nickel solubility to 8.31 ppm, compared to 30.35 ppm for pure NiO and 12.71 ppm for Co-coated NiO, highlighting the strong stabilizing effect of lithium enrichment and improved interfacial bonding (Figure 12).

Milewski et al. [71] explored the use of waste electrical and electronic equipment (WEEE) to fabricate MCFC cathodes by incorporating recycled noble, semiprecious, and rare earth metals recovered from WEEE. As MCFC components tolerate ceramic and metal impurities, using recovered noble metals as catalysts is economically viable. Their experimental results showed that MCFC cathodes containing 20% recycled electronic scrap (powder 4/1) performed better at 550°C and exhibited comparable performance to a reference cell at 650°C (1.01 V open circuit voltage). This approach supports sustainable energy and the circular economy by reducing reliance on virgin materials and minimizing electronic waste.

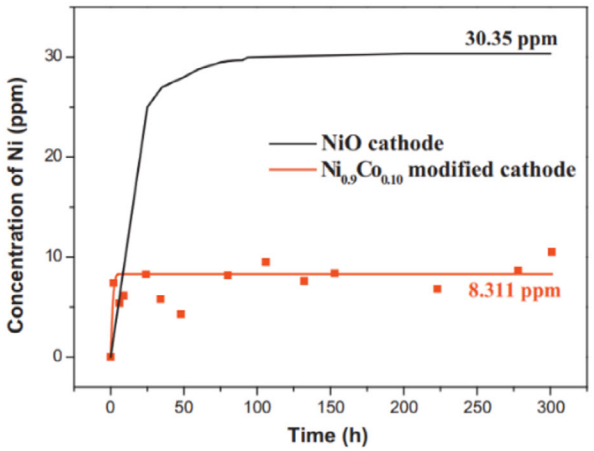

FIGURE 12 | The solubility of pristine NiO and $Ni_{0.9}Co_{0.1}O$ cathodes in $(Li_{0.62}K_{0.38})_2CO_3$ at 650°C under a CO_2/O_2 atmosphere of 0.67/0.33 atm for 300 h. Reproduced from Ref. [70]. Copyright (2011) with permission from Elsevier.

2.3 | Modification of Electrolytes

Several studies have highlighted that the choice of carbonate electrolyte plays a decisive role in controlling NiO dissolution. In particular, Li/K-based electrolytes generally exhibit higher nickel solubility than Li/Na systems, despite their superior low-temperature electrochemical performance. This trade-off between ionic conductivity and cathode stability represents a key design constraint for long-term MCFC operation [72].

A recent review on molten carbonate corrosion further supports this interpretation by emphasizing the key role of melt basicity and CO_2 partial pressure in controlling NiO stability. Wang et al. described both acidic and basic dissolution pathways of NiO in molten carbonate media and showed that higher CO_2 partial pressure can promote acidic dissolution of NiO-based surface scales. They also highlighted that, in MCFC-related studies, alkaline-earth carbonate additives such as $CaCO_3$ and $SrCO_3$ can increase melt basicity and reduce NiO solubility. These findings confirm that electrolyte chemistry and gas atmosphere are key variables in strategies aimed at suppressing NiO cathode dissolution [73].

Another effective approach to mitigate NiO dissolution in MCFC cathodes is electrolyte modification, achieved by introducing controlled amounts of alkali, alkaline earth, or rare-earth oxides and carbonates into molten alkali carbonate electrolytes without compromising electrochemical performance. Doyon et al. [74] demonstrated that the addition of 1 wt.% SrO to a Li_2CO_3–K_2CO_3 electrolyte reduced NiO solubility by a factor of 15, highlighting the strong stabilizing effect of alkaline earth oxides.

Subsequent studies confirmed that alkaline earth additives primarily act by modifying the acid–base properties of the molten carbonate. Tanimoto et al. [75] reported that Ca-, Sr-, and Ba-containing electrolytes can maintain or even enhance ionic conductivity, particularly in Li_2CO_3–Na_2CO_3 systems. Similarly, Scaccia et al. [76] showed that MgO and mixed $SrCO_3$–$BaCO_3$ additions significantly reduce NiO solubility in binary and ternary carbonate melts, with Li/Na/K/MgO systems exhibiting solubility levels comparable to highly alkaline Li–Na electrolytes.

Beyond solubility control, alkali metal additives have been investigated to improve cathode kinetics. Meléndez-Ceballos et al. [77] showed that while Li–K electrolytes outperform Li–Na below 600°C, they suffer from higher nickel solubility. The introduction of cesium enhanced oxygen reduction kinetics by increasing CO_2 diffusivity and lowering charge-transfer resistance, suggesting a superoxide-dominated mechanism. Follow-up studies incorporating Cs_2CO_3 and Rb_2CO_3 into Li–K electrolytes confirmed substantial reductions in total cell resistance, particularly for rubidium-containing systems [47, 78].

Electrolyte composition also plays a critical role in long-term stability. Lee et al. [79] compared Li–K and Li–Na electrolytes at 800°C, reporting similar initial performance but markedly

superior durability for Li–Na systems, which exhibited lower electrolyte loss rates and stable impedance over extended operation. Overall, electrolyte modification represents a powerful tool to suppress NiO dissolution and extend MCFC lifetime; however, excessive oxide additions may adversely affect performance, and potential toxicity and long-term stability of modified electrolytes require further investigation.

A comprehensive kinetic interpretation of alkali-metal additives has been provided through detailed electrochemical studies, showing that cesium and rubidium additions not only reduce NiO solubility but also alter oxygen reduction pathways by enhancing CO_2 transport and stabilizing superoxide intermediates. These effects collectively contribute to improved cathode stability and reduced polarization losses [77, 78].

To facilitate comparison among the different stabilization strategies discussed in the literature, Table 1 summarizes the main experimental conditions and performance indicators reported for NiO-based MCFC cathodes, including strategy, material, operating conditions, duration of the test, Ni solubility/precipitation values, and voltage effect.

2.4 | Synergies and Trade-Offs in Cathode–Electrolyte–Matrix Design

Recent studies indicate that NiO cathode durability cannot be interpreted only as a function of cathode chemistry but should be considered as the result of coupled interactions among electrode microstructure, electrolyte distribution, gas transport, operating atmosphere, and matrix stability. From this perspective, the cathode, electrolyte, and matrix should not be optimized independently, because a modification that improves one degradation pathway may introduce penalties in another part of the cell.

Microstructural optimization is one example of this coupled degradation behavior. Wejrzanowski et al. showed that porosity and pore size distribution are key parameters for MCFC electrodes because they affect electrolyte infiltration, gas accessibility, and fuel cell power density [59]. Similarly, layered cathode concepts based on porous Ag, NiO, and Ni foam were investigated by Ćwieka et al., who reported that the porous Ag layer decreased charge-transfer resistance, whereas the Ni foam decreased mass-transfer resistance [58]. These results do not directly quantify NiO dissolution, but they demonstrate that cathode architecture affects electrochemical losses and transport phenomena, which in turn influence the local chemical environment where NiO dissolution and nickel migration occur.

Coating-based strategies should also be interpreted in terms of both benefits and trade-offs. For example, Kim et al. proposed an atomic-layer-deposited ZrO_2 coating on the cathode and reported improved single-cell stability, which was attributed to the inhibition of NiO sintering by the ZrO_2 coating layer [51]. The same study highlights the advantage of ALD in producing uniform and thin coatings with precise thickness control. However, the protective effect of a coating must be balanced against possible limitations in gas transport, electrolyte accessibility, and active reaction area. Therefore, coating thickness, coating continuity, chemical stability, and preservation of the porous cathode structure should be considered critical design parameters when comparing coating strategies.

Potential synergies may arise when different stabilization approaches are combined. For instance, a protective coating or core–shell cathode architecture could reduce direct contact between NiO and molten carbonate, while an optimized pore-size distribution could maintain gas transport and electrolyte retention. Similarly, electrolyte modification could reduce NiO solubility, but its effectiveness would depend on matrix stability and on the ability of the matrix to control carbonate redistribution and nickel-species migration. In this sense, cathode stabilization cannot be separated from electrolyte management and matrix design.

The electrolyte and the matrix are especially important because they determine the transport path of dissolved nickel species. The manuscript already discusses that NiO dissolution is governed by the acid–base equilibrium of molten carbonates and is promoted under high CO_2 partial pressure. Dissolved nickel species may subsequently migrate through the electrolyte-filled matrix and precipitate as metallic nickel, causing internal short-circuiting [19–24]. Recent matrix-focused reviews further support this integrated view, identifying electrolyte management, matrix degradation, and matrix stability as central issues for MCFC durability [29, 30].

The main trade-offs emerging from the literature involve stability, performance, cost, and manufacturability. Protective coatings can improve cathode stability, but they require precise control of thickness and may increase processing complexity. Alternative or modified cathode compositions can reduce degradation phenomena, but they may introduce higher material cost or uncertain long-term compatibility with molten carbonates. Highly porous or layered electrodes can improve gas transport and reduce polarization losses, but excessive porosity may weaken mechanical integrity or compromise electrolyte retention. Electrolyte and matrix modifications can reduce nickel transport and precipitation, but they must remain compatible with carbonate conductivity, capillary retention, and long-term chemical stability.

3 | Summary and Outlook

MCFC technology is advancing rapidly and presents significant commercialization potential. However, increasing power density and addressing material-related challenges, particularly cathode dissolution, remain critical for widespread adoption. Improving cathode stability through material substitution, NiO doping, or coating strategies has been extensively investigated. Techniques such as atomic ALD show promise by enhancing mechanical stability and coating–substrate adhesion.

Electrolyte modification, including the addition of alkaline or rare-earth oxides, can further suppress NiO dissolution and improve performance. Careful optimization is necessary to avoid adverse effects on electrochemical activity, cost, and potential toxicity. Future research should focus on developing robust,

TABLE 1 | Comparative summary of the main strategies proposed to mitigate NiO dissolution in molten carbonate fuel cell (MCFC) cathodes.

Ref	Strategy	Material	Operating conditions	Test duration	Ni solubility / Ni precipitation	Voltage effect
[31]	Conventional coatings	Ni-Ce	Temperature: 650°C Pressure/electrolyte: Li_2CO_3/K_2CO_3, 62/38 mol% Anode gas composition: $N_2/H_2/CO_2 = 33/40/27$ mL min^{-1}, humidified at 65 °C Cathode gas composition: $N_2/O_2/CO_2 = 20/20/40$ mL min^{-1}, humidified at 35 °C	∼2100 h	Post-test SEM–EDX showed much less Ni accumulation in the electrolyte/matrix for Ni–Ce than for commercial Ni; dissolution reduction is qualitative, not given as ppm	Commercial Ni decreased from ∼ 0.80 to 0.72 V at 150 mA cm^{-2} over 1000 h Ni–Ce remained around 0.68 V at 200 mA cm^{-2} up to 2100 h
[32]	Conventional coatings	$LiFeO_2$–$LiCoO_2$–NiO ternary compositions	Temperature: 650°C Pressure/electrolyte: Li_2CO_3/Na_2CO_3, 52/48 mol% Anode gas composition:/ Cathode gas composition: 70% CO_2 - 30% O_2	200 h	Solubility 1.5–3.3 ppm	OCV monitored, no quantitative voltage data
[33]	Conventional coatings	LiMg0.05Co0.95O2-coated porous Ni cathode	Temperature: 650°C Pressure: 1 atm/electrolyte: Li_2CO_3/K_2CO_3, 62/38 mol% Anode gas composition: $N_2/H_2/CO_2 = 10/10/1$ NL h^{-1} Cathode gas composition: $N_2/O_2/CO_2 = 7/0/16$ NL h^{-1}	>1000 h	/	Stable voltage about 800 mV at 100 mA cm^{-2} after 700 h
[34]	Conventional coatings	CoOOH on Ni substrate	Temperature: 650°C Pressure/electrolyte: Li_2CO_3/Na_2CO_3, 52/48 mol% Anode gas composition: /Cathode gas	48 h	Solubility $7–10 \times 10^{-5}$ mol kg^{-1}	OCV stabilizes at ∼–0.4 V vs Ag^+/Ag
[35]	Conventional coatings	CoO/NiO composite cathodes	Temperature: 650°C Pressure/electrolyte: Li_2CO_3/K_2CO_3, 62/38 mol% Anode gas composition:/ Cathode gas composition: 30% CO_2 - 70% air	400 h	5 mass% CoO composite: Ni solubility reduced to ∼ 2/3 of NiO	/

(Continues)

TABLE 1 | (Continued)

Ref	Strategy	Material	Operating conditions	Test duration	Ni solubility / Ni precipitation	Voltage effect
[36]	Conventional coatings	$LiCoO_2$-coated NiO cathode	Temperature: 650°C Pressure/electrolyte: Li_2CO_3/K_2CO_3, 62/38 mol% Anode gas composition:/ Cathode gas composition: 30% CO_2 - 70% air	300 h	LC-NiO solubility about half that of NiO after 300 h	OCV about 1.1 V; CCV about 0.85 V vs 0.80 V for NiO at 150 mA cm^{-2}
[37]	Conventional coatings	TiO_2-coated Ni cathode	Temperature: 650°C Pressure/electrolyte: Li_2CO_3/K_2CO_3, 62/38 mol%	250 h	SolubilityPure NiO: 30.35×10^{-6} mole fractionTiO_2 2.5 mol%: 17.82×10^{-6} mole fractionTiO_2 5 mol%: 6.86×10^{-6} mole fraction	/
[39]	Conventional coatings	Co/Ce-coated Ni cathodes	Temperature: 650°C Pressure/electrolyte: Li_2CO_3/K_2CO_3, 62/38 mol% Anode gas composition:/ Cathode gas composition: 67% CO_2 - 33% O_2	300 h	SolubilityPure NiO: 30.35×10^{-6} mole fractionCo-coated: 12.71×10^{-6} mole fractionCo/Ce 9.5/0.5: 5.54×10^{-6} mole fraction	/
[40]	Conventional coatings	$LiCoO_2$-coated NiO cathodes	Temperature: 650°C Pressure: 1–5 atm Electrolyte: Li_2CO_3/K_2CO_3, 70/30 mol% Anode gas composition: 72% H_2 - 18% CO_2 - 10% H_2O Cathode gas composition: 30% CO_2 - 70% air	1000 h	Ni precipitation in matrix after 1000 h: NiO cathode = 3.2 wt% (1 atm), 5.2 wt% (3 atm), 8.6 wt% (5 atm); $LiCoO_2$-coated cathodes reduced values to 1.4 wt% (1 atm), 2.9 wt% (3 atm), 7.4 wt% (5 atm)	Cell voltage/performance comparable to conventional NiO cathode at 1, 3, and 5 atm with no significant decay during 1000 h
[41]	Conventional coatings	$LiCoO_2$-coated NiO cathodes	Temperature: 650°C Pressure: 1 atm Electrolyte: Li_2CO_3/K_2CO_3 70/30 mol% Anode gas composition: 72% H_2 - 18% CO_2 - 10% H_2O Cathode gas composition: 30% CO_2 - 70% air	1000 h	Coating significantly reduced Ni deposition in matrix (no quantitative data)	Standard NiO cell: ∼0.85 VCoated cathodes > 0.8 V after ∼ 200 h;
[47]	ALD coatings	ALD TiO_2-coated Ni cathode	Temperature: 650°C Pressure /electrolyte: Li_2CO_3/K_2CO_3, 62/38 mol% Anode gas composition:/ Cathode gas composition:/	230 h	ALD TiO_2 coating reduced Ni solubility from ∼ 15 to ∼ 8 wt.-ppm	/

(Continues)

TABLE 1 | (Continued)

Ref	Strategy	Material	Operating conditions	Test duration	Ni solubility / Ni precipitation	Voltage effect
[48]	ALD coatings	ALD TiO_2 (50 and 300 nm)	Temperature: 650°C Pressure: 1 atm Electrolyte: Li_2CO_3/K_2CO_3 62/38 mol% Anode gas composition:/ Cathode gas composition: 30% CO_2 - 70% air	230 h	Solubility Ni: 15 ppm TiO_2 50 nm: 8.2 ppm TiO_2 300 nm: 11.1 ppm	TiO_2 coatings delayed stabilization of oxygen reduction equilibrium
[49]	ALD coatings	ALD CeO_2 (27 and 127 nm)	Temperature: 650°C Pressure: 1 atm Electrolyte: Li_2CO_3/K_2CO_3 62/38 mol% Anode gas composition:/ Cathode gas composition: 30% CO_2 - 70% air	230 h	Solubility Ni: 15 ppm CeO_2 27 nm: 10 ppm CeO_2 127 nm: 8 ppm	Ni reached oxygen reduction plateau (∼−0.03 V vs Ag/Ag^+) after ∼ 182 h CeO_2 coatings delayed Ni oxidation/lithiation by ∼ 30–110 h.
[50]	ALD coatings	ALD Nb_2O_5 (5, 20, 50 and 300 nm)	Temperature: 650°C Pressure: 1 atm Electrolyte: Li_2CO_3/K_2CO_3 62/38 mol% Anode gas composition:/ Cathode gas composition: 30% CO_2 - 14% O_2 - 56% Ar	230 h	Solubility Ni: 15 ppmNb_2O_5 20 nm: 10 ppm	20 nm Nb_2O_5 coating reached stable ORR potential (∼0.07 V vs Ag/Ag^+) after ∼ 79 h, about 112 h earlier than bare Ni (∼182 h) 50 nm coating stabilized at ∼ 0.05 V after ∼ 187 h
[51]	ALD coatings	ALD ZrO_2 (∼2 nm)	Temperature: 600°C Pressure/electrolyte: Li_2CO_3/K_2CO_3, 62/38 mol% Anode gas composition: 80% H2 - 20% CO2 Cathode gas composition: 30% CO_2 - 70% air	350 h	Solubility Ni concentration after 150 h: uncoated cathode ∼ 6 ppm ZrO_2-coated cathode ∼ 7 ppm	At 150 mA cm^{-2}: uncoated cell = 0.837 V; ZrO_2-coated cell = 0.867 V. During 2000 h test, coated cell remained stable while uncoated cell degraded after ∼ 1300 h
[52]	Conventional coatings	Nano-size Co_3O_4 coating on Ni	Temperature: 650°C Pressure/electrolyte: Li_2CO_3/K_2CO_3, 62/38 mol% Anode gas composition:/ Cathode gas composition: 67% CO_2 - 33% O_2	300 h	Solubility NiO cathode: 3.035×10^{-5} mol fraction Co-coated Ni cathode: 1.271×10^{-5} mol fraction	OCV ≈ 1.1 V for both cells CCV at 150 mA cm^{-2}: NiO = 0.80 V, Co-coated Ni = 0.82 V

(Continues)

TABLE 1 | (Continued)

Ref	Strategy	Material	Operating conditions	Test duration	Ni solubility / Ni precipitation	Voltage effect
[53]	Conventional coatings	LiMg0.05Co0.95O2 precursor coating (sol–gel derived)	Temperature: 650°C Pressure: 1 atm Electrolyte: Li_2CO_3/K_2CO_3 62/38 mol% Anode gas composition:/ Cathode gas composition: /	1000 h	Ni precipitation in matrix directly observed by SEM/EDS	OCV ≈ 1.1 V; stable operation at 55–160 mA cm^{-2}
[54]	Conventional coatings	$LiCoO_2$ coating (140–640 µm)	Temperature: 650°C Pressure/electrolyte: Li_2CO_3/K_2CO_3, 62/38 mol% Anode gas composition:/ Cathode gas composition: 67% CO_2 - 33% O_2	16,360 h	NiO solubility at Ni/NiO equilibrium ≈ 6.2 mol ppm in Li/K melt Ni deposition in matrix strongly reduced by $LiCoO_2$ coatings; 620 µm coating reduced Ni transfer by > 5× vs uncoated NiO cathode	$LiCoO_2$ coatings reported to exhibit oxygen reduction overpotentials comparable or lower than lithiated NiO cathodes
[55]	Conventional coatings	Nanosized $LiCoO_2$ coating (20–140 µm; 10–25 wt%)	Temperature: 600°C Pressure/electrolyte: Li_2CO_3/K_2CO_3, 62/38 mol% Anode gas composition: 72% H2 - 18% CO2 - 10 H2O Cathode gas composition: 30% CO_2 - 70% air	>700 h	Solubility Uncoated Ni cathode: 24.4 µg g^{-1} dissolved Ni $LiCoO_2$ pellet: 0.27 µg g^{-1} dissolved Co	Uncoated cathode: 0.838 V at 150 mA cm^{-2} $LiCoO_2$-coated cathodes: 0.878 V (10 wt%), 0.889 V (15 wt%), 0.892 V (20 wt%), 0.869 V (25 wt%)
[58]	Core–shell/multilayer architectures	Layered structure: porous Ag layer + Ni foam support + NiO layer	Temperature: 650°C Pressure/electrolyte: Li_2CO_3/K_2CO_3, 62/38 mol% Anode gas composition: 80% H2 - 20% CO2 Cathode gas composition: 30% CO_2 - 70% air	/	/	OCV ≈ 0.87 V; maximum power density = 249 mW cm^{-2} vs 151 mW cm^{-2} for standard NiO cathode
[59]	Core–shell/multilayer architectures	Two-layer cathode: low-porosity top layer (55%) + high-porosity bottom layer (63%)	Temperature: 650°C Pressure/electrolyte:/ Anode gas composition: 80% H2 - 20% CO2 Cathode gas composition: 30% CO_2 - 70% air	1000 h	/	Thin low-porosity layer (100 µm) slightly increased maximum power density compared with homogeneous cathode

(Continues)

TABLE 1 | (Continued)

Ref	Strategy	Material	Operating conditions	Test duration	Ni solubility / Ni precipitation	Voltage effect
[60]	Conventional coatings	Porous Ag layer	Temperature: 650°C Pressure/electrolyte Anode gas composition: 80% H2 - 20% CO2 Cathode gas composition: 30% CO_2 - 70% air	1000 h	/	<4% voltage drop after 1000 h; improved cell performance vs standard NiO cathode
[61]	Conventional coatings	Ag coating (0.8 and 3 wt% nano-Ag)	Temperature: 550°C-650°C Pressure/electrolyte: Li_2CO_3/K_2CO_3, 62/38 mol% Anode gas composition: 72% H2 - 18% CO2 - 10 H2O	600 h	/	At 600 °C and 150 mA cm^{-2}: uncoated = 0.76 V 0.8 wt% Ag = 0.77 V 3 wt% Ag = 0.80 V At 620 °C: uncoated = 0.80 V 3 wt% Ag = 0.83 V
[62]	Conventional coatings	LSCF coating (La0,6 Sr0,4Co0,2Fe0,8O_3, 1.8 and 5.2 wt%)	Temperature: 600°C–700°C Pressure/electrolyte: Li_2CO_3/K_2CO_3, 62/38 mol% Anode gas composition: 72% H2 - 18% CO2 - 10 H2O Cathode gas composition: 30% CO_2 - 70% air	>2000 h	/	At 650 °C and 150 mA cm^{-2} uncoated = 0.805 V 5.2 wt% LSCF = 0.837 V
[63]	Conventional coatings	Nano-sized $LiNiO_2$ layer (5–20 wt%)	Temperature: 580°C–650°C Pressure:/ Cathode gas composition: 30% CO_2 - 70% air	>2000 h	/	At 600 °C and 150 mA cm^{-2}: uncoated = 0.81 V 10 wt% $LiNiO_2$ = 0.87 V
[64]	Alternative cathode materials	TiO_2/Ag nanocomposite deposited by electrophoretic deposition (EPD)	Temperature: 650°C Pressure/electrolyte: Li_2CO_3/K_2CO_3, 62/38 mol% Anode gas composition: 80% H2 - 20% CO2 Cathode gas composition: 30% CO_2 - 70% air	200 h	Solubility Reference cathode $\approx 3.93 \times 10^{-5}$ mole fraction TiO_2/Ag-coated cathode $\approx 3.0 \times 10^{-5}$ mole fraction	/

(Continues)

TABLE 1 | (Continued)

Ref	Strategy	Material	Operating conditions	Test duration	Ni solubility / Ni precipitation	Voltage effect
[65]	Alternative cathode materials	BYS coating (Bi1,5Y0,3Sm0,3O3−δ mixed ionic/electronic conductor, ∼5.9–9.5 wt%)	Temperature: 550°C–650°C Pressure: 1 atm Electrolyte: Li_2CO_3/Na_2CO_3 52/48 mol% Anode gas composition: 72% H2 - 18% CO2 - 10 H2O Cathode gas composition: 30% CO_2 - 70% air	1000 h	/	At 550 °C and 150 mA cm^{-2}: conventional cathode could not operate; BYS-coated cathode achieved 0.501 V
[66]	NiO doping	La-modified NiO	Temperature: 650°C Pressure:/electrolyte: Li_2CO_3/K_2CO_3, 62/38 mol% Anode gas composition: 67% H2 - 33% CO2 Cathode gas composition: 30% CO_2 - 70% air	600 h	Solubility NiO: ∼38.95 ppm Ni after 300 h 0.5 mol% La: 8.678 ppm	NiO: OCV 1.06 V, CCV 0.87 V @150 mA cm^{-2} 0.5 mol% La: OCV 1.07 V, CCV 0.95 V @150 mA cm^{-2}
[68]	Core–shell / multilayer architectures	Two-layer cathode: low-porosity top layer (55%) + high-porosity bottom layer (63%)	Temperature: 650°C Pressure /electrolyte: / Anode gas composition: 80% H2 - 20% CO2 Cathode gas composition: 30% CO_2 - 70% air	/	/	OCV reached ∼ 1.1 V after start-up
[71]	NiO doping	20 wt% recycled WEEE-derived powder (KREC41: Ce/Zr-rich; KREC42: Ag-rich fraction)	Temperature: 550°C–650°C Pressure:/electrolyte: Li_2CO_3/K_2CO_3, 62/38 mol% Anode gas composition: $H_2/CO_2 = 33/56/13{,}5$ mL min^{-1} Cathode gas composition: air/$CO_2 = 142/54$ mL min^{-1}	/	/	At 650 °C and maximum flow: reference and KREC41 both ≈1.01 V OCV and 0.13 A cm^{-2} max current density; KREC42: 0.97 V OCV and 0.09 A cm^{-2}. At 550 °C, KREC41 clearly outperformed reference cell
[74]	Electrolyte modification	Addition of alkaline earth oxides (MgO, SrO) to Li_2CO_3–K_2CO_3 eutectic (62/38 mol%)	Temperature: 650°C Pressure: /electrolyte: Li_2CO_3/K_2CO_3, 62/38 mol% Anode gas composition: / Cathode gas composition: /	200 h	Minimum NiO solubility ≈ 18 ppb at $PCO_2 \approx 10^{-3}$ atm	/

(Continues)

TABLE 1 | (Continued)

Ref	Strategy	Material	Operating conditions	Test duration	Ni solubility / Ni precipitation	Voltage effect
[75]	Electrolyte modification	Addition of alkaline earth carbonates ($CaCO_3$, $SrCO_3$, $BaCO_3$ up to 17 mol%) to Li_2CO_3–Na_2CO_3 eutectic (52/48 mol%)	Temperature: 650°C Pressure/electrolyte: Li_2CO_3/Na_2CO_3 52/48 mol% Anode gas composition:/ Cathode gas composition:/	650 h	Baseline Li/Na electrolyte: $\sim 18 \times 10^{-6}$ mole fraction NiO NiO solubility decreased monotonically with alkaline earth carbonate addition	/
[76]	Electrolyte modification	Binary and ternary carbonate electrolytes: Li/K, Li/Na, Li/Na/K + additives (MgO, $SrCO_3$, $BaCO_3$)	Temperature: 650°C Pressure/electrolyte: Li/K, Li/Na, Li/Na/K Anode gas composition:/ Cathode gas composition: 67% CO_2 - 33% O_2	100 h	Solubility Li/K = 30 mol ppm Li/Na = 12 mol ppmLi/Na = 9 mol ppm Li/Na/K = 20 mol ppm 3 mol% MgO reduced solubility by ∼ 40% in Li/K and ∼ 20% in Li/Na 3 mol% ($SrCO_3$+$BaCO_3$) reduced NiO solubility in Li/Na electrolyte by ∼ 50%	/
[78]	Electrolyte modification	5 mol% Cs_2CO_3 or Rb_2CO_3 added to Li_2CO_3/K_2CO_3 (62/38) and 5 mol % Cs_2CO_3 added to Li_2CO_3/Na_2CO_3 (52/48)	Temperature: 650°C Pressure/electrolyte: Li_2CO_3/K_2CO_3, 62/38 mol% and Li_2CO_3/Na_2CO_3, 52/48 mol% Anode gas composition:/ Cathode gas composition: 30% CO_2 - 14% O_2 - 56% Ar	224 h	/	In Li/K electrolyte Cs reduced total resistance from ∼ 358 Ω to ∼ 40 Ω Rb reduced it to ∼ 111 Ω
[79]	Electrolyte modification	Electrolyte-impregnated matrix and cathode using $(Li/Na)_2CO_3$ eutectic (52/48 mol%)	Temperature: 550°C–650°C Pressure/electrolyte: Li_2CO_3/Na_2CO_3, 52/48 mol% Anode gas composition: 72% H2 - 18% CO2 - 10 H2O Cathode gas composition: 30% CO_2 - 70% air	1000 h	/	At 160 mA cm^{-2}: 0.860 V (650 °C) 0.835 V (620 °C) 0.802 V (600 °C) 0.749 V (580 °C) 0.641 V (550 °C)

TABLE 2 | Comparison of strategies to mitigate NiO dissolution in MCFC cathodes.

Strategy	Representative materials/methods	Reduction of Ni dissolution	Impact on electrochemical performance	Scalability & cost	TRL	Key limitations	Reference
NiO doping	Co-, La-, Ti-doped NiO	Moderate (30%–50%)	Usually neutral or positive (↑ conductivity, ORR activity)	High scalability, low–moderate cost	4–5	Limited long-term suppression at high CO_2 pressure	[56, 66, 71]
Conventional coatings	$LiCoO_2$, Co_3O_4, Ag, $LiNiO_2$ (sol–gel, impregnation, Pechini)	High (up to ~ 60%)	Slight initial voltage penalty possible; stable long-term	Scalable, industrially mature	5–6	Thickness/porosity optimization critical	[31–41, 52–55, 60–63]
ALD coatings	TiO_2, ZrO_2, CeO_2 (ALD)	High (≈50%–60%)	Generally preserved ORR kinetics; excellent stability	Currently higher cost, emerging scale-up	3–4	Equipment cost, deposition time	[47–51]
Alternative cathode materials	$LiCoO_2$, $LiFeO_2$, BYS, perovskites	Very high (order-of-magnitude lower solubility)	Often limited by low ORR kinetics	Moderate–low scalability	3–4	Trade-off between stability and activity	[64, 65, 69]
Core–shell/ multilayer architectures	NiO–$LiCoO_2$, Ni–foam supported cathodes	Very high (down to ~ 8 ppm Ni)	Improved gas diffusion and mechanical stability	Moderate scalability	4–5	Fabrication complexity	[58, 59, 68, 71]
Electrolyte modification	SrO, CaO, MgO, Cs_2CO_3, Rb_2CO_3	Very high (up to 15× reduction)	Can improve ORR kinetics if optimized	High scalability, low material cost	5–6	Risk of conductivity loss or toxicity	[47, 74–79]

scalable, and cost-effective materials while integrating advanced coating techniques and novel electrolyte additives.

Overall, combining improved cathode materials, advanced coatings, and optimized electrolytes represents a comprehensive strategy to enhance MCFC durability and efficiency. Continued experimental and computational studies are essential to guide the design of next-generation MCFCs, aiming for higher stability, lower cost, and sustainable deployment in energy systems.

The long-term durability of MCFCs is fundamentally limited by the dissolution of NiO cathodes in molten carbonate electrolytes, which leads to nickel precipitation, internal short-circuiting, and accelerated voltage decay. Addressing this degradation mechanism remains a prerequisite for extending MCFC lifetime toward commercially relevant targets.

Among cathode-centered approaches, NiO doping and conventional coating strategies, such as $LiCoO_2$–, Co_3O_4–, and Ag-based layers currently represent the most practical solutions. These methods have repeatedly demonstrated substantial reductions in nickel dissolution (typically up to ~60%) while relying on fabrication routes that are already compatible with large-scale electrode manufacturing.

More advanced surface-engineering techniques, particularly atomic ALD, provide superior control over coating thickness and interfacial quality, resulting in excellent chemical stability without severely compromising oxygen reduction kinetics. Despite the higher cost and complexity of ALD processes, their ability to produce highly uniform and durable coatings makes them especially attractive for future high-performance MCFC designs.

Complete replacement of NiO with alternative cathode materials remains difficult. Although compounds such as $LiCoO_2$, $LiFeO_2$, and BYS exhibit intrinsically lower solubility in molten carbonates, their implementation is often constrained by reduced catalytic activity or demanding processing conditions. In this context, hybrid solutions such as core shell structures and multilayer cathodes appear particularly effective, as they allow electrochemical activity and chemical stability to be optimized independently.

Electrolyte modification represents a complementary and highly impactful strategy. The addition of alkaline or alkaline-earth oxides (e.g., SrO, CaO, and MgO), as well as alkali carbonates such as Cs_2CO_3 and Rb_2CO_3, has been shown to suppress NiO dissolution by more than an order of magnitude. However, these benefits must be balanced against potential drawbacks related to ionic conductivity, long-term electrolyte stability, and environmental considerations.

Overall, the evidence reviewed in this article indicates that no single modification is sufficient to fully address NiO degradation. The comparison reported in Table 2 highlights that no single strategy fully resolves the trade-off between cathode stability, electrochemical activity, scalability, and cost, confirming that combined approaches are likely required for durable commercial MCFC operation. Rather, the most robust pathway toward long-lived MCFCs lies in the combined optimization of stabilized NiO cathodes, electrode architecture, and electrolyte composition. Future efforts should therefore focus on integrated cathode–electrolyte design, supported by targeted experiments and modeling, to achieve operational lifetimes exceeding 40,000 h under realistic operating conditions.

Future validation should therefore be extended to commercially relevant conditions, including large-area stack operation, pressurized environments, realistic flue-gas impurities, electrolyte redistribution or loss, and repeated thermal cycling [25–30]. Particular attention should also be paid to reducing cobalt dependence and developing scalable, low-cost cathode and electrolyte modification routes suitable for long-term industrial MCFC operation.

Acknowledgments

This research was partially funded by the project CALIPSO - Celle a combustibile innovative ad alta potenza in sistemi stazionari e di mobilità. PNRR – Prog. n. RSH2A_000021-CUP: F57G25000200006.

Open access publishing facilitated by Universita degli Studi di Genova, as part of the Wiley-CRUI-CARE agreement.

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

Data sharing is not applicable to this article, as no datasets were generated or analyzed during the current study.

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