ELECTROCHEMICAL DEGRADATION MECHANISMS IN MOLTEN CARBONATE FUEL CELLS AND STRATEGIES FOR CORROSION MITIGATION

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Molten carbonate fuel cells (MCFCs) offer high efficiency and fuel flexibility, but they suffer from corrosion of metallic components, particularly current collectors. This work examines degradation mechanisms of Fe-, Cr-, and Ni-based alloys under MCFC conditions, highlighting oxide dissolution and spinel growth that increase ASR. Advanced strategies, including alloying and coatings (CrN, TiN, TiAlN, Co-Cr, Cu-Ni-Zn-Fe), are discussed as pathways to improve durability and enable liquid-fuel MCFC applications.

Keywords: molten carbonate fuel cells, corrosion, protective coatings, nitrides, spinels, current collectors, electrochemical degradation

Introduction. Molten carbonate fuel cells (MCFCs) offer electrical efficiencies up to 60% and can operate directly on natural gas, syngas, or bio-derived fuels. Their tolerance to carbon dioxide makes them suitable for integration with carbon capture and utilization technologies. Nevertheless, widespread application is hindered by degradation of metallic components, particularly current collectors and bipolar plates, which directly limits system lifetime and increases costs [1–2].

The objective of this study is to elucidate the electrochemical degradation pathways in MCFCs, focusing on the reactions of Fe, Cr, and Ni under operating conditions, and to present strategies for mitigating corrosion through alloy engineering and protective coatings [3–5]. Special emphasis is placed on solutions compatible with liquid-fuel MCFCs, which demand both chemical stability and catalytic activity [6].

Results and discussion. *Degradation of Austenitic Stainless Steels in MCFCs.* Conventional steels such as 304 and 316L initially form protective Cr_2O_3 layers [7]. Under MCFC conditions, these layers degrade due to reaction wit lithium and conversion into soluble chromates, while Fe oxides form lithium ferrites ($LiFeO_2$, $LiFe_5O_8$). The net result is chromium depletion, loss of passivation, and growth of mixed spinel layers ($(Fe,Ni)Cr_2O_4$), which increase *area-specific resistance* (ASR) [8]. Stainless steel 316L shows improved resistance compared to 304 due to Mo additions but remains vulnerable to long-term degradation. Advanced steels containing Mn or Al (e.g., Nitronic alloys, Fe–Cr–Al compositions) form alternative protective layers such as $LiMn_2O_4$ or $LiAlO_2$. However, these often suffer from poor electrical conductivity, limiting their application in current-carrying components [9].

Fundamental Reactions of Oxidation and Dissolution. Initial thermal oxidation of metallic substrates leads to the formation of protective oxides:

- *Iron:*

$$Fe + \tfrac{1}{2}O_2 \rightarrow FeO \quad (1)$$

$$Fe + \tfrac{2}{3}O_2 \rightarrow \tfrac{1}{3}Fe_3O_4 \quad (2)$$

$$Fe + \tfrac{3}{4}O_2 \rightarrow \tfrac{1}{2}Fe_2O_3 \quad (3)$$

- *Chromium:*

$$Cr_2O_3 + CO_3^{2-} \rightarrow 2CrO_4^{2-} + \tfrac{1}{2}O_2 + CO_2 \quad (4)$$

However, in molten carbonate environments, these oxides undergo secondary reactions with Li_2CO_3:

$$Fe_2O_3 + Li_2CO_3 \rightarrow 2LiFeO_2 + CO_2\uparrow \quad (5)$$

$$Cr_2O_3 + 2Li_2CO_3 + 3/2O_2 \rightarrow 2Li_2CrO_4 + 2CO_2\uparrow \quad (6)$$

Nickel, whether from stainless steel or the NiO cathode, can form stable lithium nickelates:

$$Ni + CO_3^{2-} + O^{2-} \rightarrow LiNiO_2 \quad (7)$$

Yet, NiO is partially soluble in molten carbonate, leading to the migration of Ni^{2+} species into the electrolyte and subsequent unwanted deposition at the anode side, often resulting in internal short-circuiting.

Protective Coatings and Advanced Mitigation Strategies. Recent research has focused on barrier and catalytic coatings:

- CrN and TiN coatings form conductive, stable ceramic layers with low ASR (~20 $m\Omega\cdot cm^2$) and significantly reduced corrosion rates. Multilayer systems (CrN/TiN) improve mechanical durability.
- TiAlN coatings exploit the formation of $LiAlO_2$ from Al_2O_3, which is chemically resistant to molten carbonates.
- Co–Cr coatings generate spinel $CoCr_2O_4$, reducing chromium volatilization while forming $LiCoO_2$ in contact with lithium carbonate, a phase stable in the electrolyte.
- Cu–Ni–Zn–Fe coatings combine passivating CuO layers with conductive spinels ($NiFe_2O_4$, $CuFe_2O_4$), offering an alternative low-cost solution.

These coatings are typically assessed using ASR measurements, electrochemical impedance spectroscopy (EIS), and microstructural methods (SEM/EDS), which provide insight into corrosion kinetics and protective layer morphology.

The current NATO-supported project focuses on developing Liquid Fuel MCFCs (LF-MCFCs) with functional coatings that act simultaneously as corrosion barriers and catalysts for liquid fuel reforming. The target outcomes include:

- Fuel utilization ≥50%,
- Lifetime improvement of ≥15% with protective coatings,
- Power density ≥75 mW/cm^2.

This approach not only addresses the fundamental problem of material degradation but also enables direct use of liquid fuels such as ethanol and methanol, which are attractive for portable and military power applications [10–11].

Conclusions. Electrochemical degradation in MCFCs arises primarily from the interaction of molten carbonates with metallic oxides, leading to lithium ferrite and chromate formation, nickel dissolution, and increased resistance of protective scales. Advanced alloying strategies and protective coatings such as nitrides, spinels, and multi-component oxides have demonstrated significant improvements in corrosion resistance and electrical stability. Integration of these materials into LF-MCFC designs provides a pathway toward durable, fuel-flexible systems with enhanced applicability in mobile and energy-security contexts.

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