REVIEW

Materials issues and recent developments in molten carbonate fuel cells

A. Kulkarni · S. Giddey

Abstract Molten carbonate fuel cell is one of the most promising high efficiency and sustainable power generation technologies, as demonstrated by the availability of several commercial units nowadays. Despite the significant progress made over the past few decades, the issues like component stability in carbonate melts and lower power density as compared to other high-temperature fuel cell systems need to be overcome to meet cost and lifetime targets. An improvement in the catalysts and system design for in situ reforming of fuel is critical to make molten carbonate fuel cells (MCFCs) compatible with real world fuels with minimal preprocessing requirements. Thus a significant opportunity exists for materials R&D in the MCFC area. In the present review, the key issues with MCFC component materials: cathode, anode, matrix, current collectors and bipolar plates, are discussed. The alternative materials and strategies adapted by the MCFC R&D community to mitigate these issues are discussed with emphasis on research trends and developments over the past decade.

Keywords Fuel cell · Molten carbonate fuel cell · MCFC · Molten carbonate electrolyte · Materials issues

Introduction

The stationary power generation with molten carbonate fuel cell (MCFC) technology offers an efficient alternative to conventional coal-fired power plants. The history of the molten carbonate fuel cell can be tracked back to the late 1950s, when Dutch scientists G.H.J. Broers and J.A.A. Ketelaar started the research on fused salt electrolytes [1]. Typically fuel cells are named after the electrolyte used in the fuel cell, and as the name suggests, molten carbonate fuel cell is based upon molten carbonate electrolyte. It is considered as an intermediate temperature fuel cell as it operates at a temperature higher than polymer electrolyte fuel cell but lower than traditional solid oxide fuel cells (SOFC), typically at 650 °C. Its ability to cope with the different fuel types such as hydrogen, natural gas, light alcohols and its operation without noble metal catalysts, distinguishes it from low temperature fuel cells. Over the last five decades, the MCFC technology has made impressive progress and a number of MCFC-based power generators are currently being demonstrated across the world. With the years of academic and industrial R&D in various countries such as USA, Japan, Korea and EU, the MCFC technology is approaching mass commercialisation. It is rather interesting that despite the issues such as materials stability in corrosive environments, and lower power densities as compared to other fuel cells, MCFC has emerged as the preferred technology when it comes to commercialised stationary power generation. Various companies worldwide are field testing kilowatt to megawatt class MCFC power generation systems. Some of these companies are also offering MCFC systems to customers such as hospitals, hotels, data centres and other industries with relatively smaller power needs such as waste water treatment plants. Other application areas such marine transportation are also being explored for MCFCs. As a result of the focused R&D and commercialization efforts, MCFC is now the leader in terms of the number of installed power generation units among all fuel cell technologies [2, 3]. Table 1 summarises the recent technology status of the major companies working in the

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MCFC area. For a detailed description of the current technology status, readers are referred to the reference [2].

Figure 1 shows the schematic of the working structure of a typical MCFC. The electrolyte mixture (molten carbonate salts) is held in the porous ceramic matrix between a porous anode and a porous cathode. At equilibrium, all matrix pores, being smaller in diameter as compared to electrode pores, are filled with electrolyte, while electrode pores are partially filled permitting diffusion of gaseous species. The partially filled pores in electrodes provide triple-phase boundaries (solid electrode, reactant gas and liquid
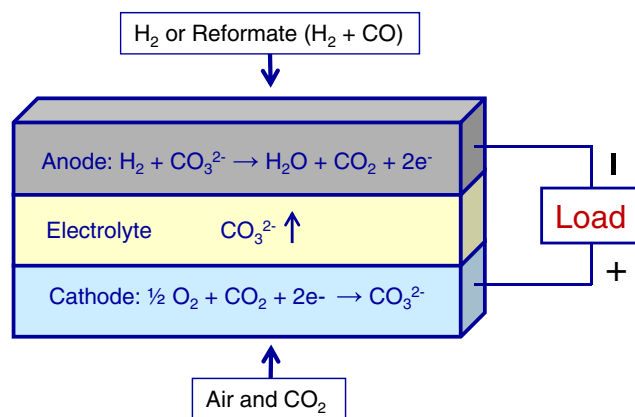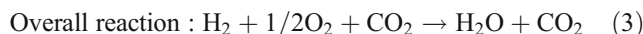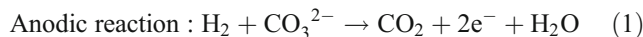

Fig. 1 A schematic of operating principle of a MCFC

electrolyte) for redox reactions. The stable electrolyte/gas interface in the MCFC electrodes is based on a capillary pressure balance inside the pores of electrodes which, in turn, depends upon surface tension of molten carbonate and the contact angle with the matrix and electrodes. The electrochemical reaction involves formation of the carbonate (CO_3^{2-}) ion at the cathode and its transport to anode via the molten carbonate mixture. At the anode, the carbonate ion is reduced by fuel (hydrogen) to form water and CO_2. The electrons produced flow through the external circuit to complete the reaction.

The electrochemical reactions are given as:

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

$$\text{Cathodic reaction}: 1/2O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-} \quad (2)$$

$$\text{Overall reaction}: H_2 + 1/2O_2 + CO_2 \rightarrow H_2O + CO_2 \quad (3)$$

The carbon dioxide required for cathodic reaction (Eq. 2) can be recycled from the anode chamber exit. The Nernst potential or open circuit voltage of a single cell is given by,

$$E = E_0 + RT/2F \ln\left[\left(p_{H_2(a)} \times p_{O_2(c)}^{1/2}/p_{H_2O(a)}\right) \cdot \left(p_{CO_2(c)}/p_{CO_2(a)}\right)\right] \quad (4)$$

Where E_0 is the voltage at standard pressure, R, T, F are, respectively, the universal gas constant, the temperature and the Faraday constant, while p_{CO_2} and p_{O_2} are partial pressures of CO_2 and O_2, respectively. In the equation, subscripts (a) and (c) denote, respectively, the anode and cathode sides of the cell. As in case of any fuel cell, the operating voltage at a particular current density is determined by the voltage losses due to the following:

Ohmic resistance: Electrolyte resistance, ohmic resistance of electrodes and contact resistances

Table 1 The commercial developers of MCFC technology and current status of their technology [2, 3]

Company	Technology features
Fuel Cell Energy, USA	• World leader in terms of installed MCFC units • 300 kW–2.8 MW units, commercially available • Combined heat and power with gas expansion turbine delivers up to 65 % efficiency • Fuels: natural gas and anaerobic digester gas with internal reforming
CFC Solution, Germany	• Hot module concept: all moving components in a single enclosure • 250 to 500 kW power. Electrical efficiency up to 50 % for AC applications • Lifetime of 30,000 h in pilots (single stack) • Fuels: sewage gas, natural gas and biogas compatible
Ansaldo Fuel Cells (AFCo), Italy	• Standardised stack components, two electrochemical modules per unit • 1 kW–MW range • 20,000 h of grid connected operation demonstrated • Validated for fuels such as diesel and coal gas • Technology in final pre-commercialization stage
Ishikawajima-Harima Heavy Industries (IHI), Japan	• Pressurised MCFCs operation • 1 MW pilot plant operated for 5,000 h • Achieved 51 % total efficiency in pilot plant • Best operation time of 16,000 h achieved • High performance stacks 1.5 kW m^{-2}
MTU Friedrichshafen, Germany	• 250 kW MCFCs commercialised for residential applications • Demonstrated 240 kW unit compatible with different fuels such as natural gas and methane
Gencell Corporation, USA	• 40–125 kW distributed power generation

Electrode polarisation: Polarisation or charge transfer reaction at anode and cathode

Concentration polarisation or mass transport losses: This type of loss is typically observed at higher currents when the diffusion of reactants or products across the pores in electrodes is not fast enough.

The actual output voltage obtained at current i, assuming no concentration polarisation losses, is given by:

$$V = E - iR_{ele} - i\eta_c - i\eta_a \qquad (5)$$

R_{ele}, η_c and η_a are the electrolyte resistance, cathodic overvoltage and anodic overvoltage, respectively. Figure 2 shows a typical polarisation curve of an MCFC compared with the V-I characteristics of other types of fuel cells [4]. It can be seen from Fig. 1 that MCFC V-I characteristics are easily distinguishable from other types of fuel cells. A typical MCFC shows V-I linear characteristics with mainly ohmic losses dominating; however, it also offers the highest efficiencies at the lower end of the current densities.

The conventional material choices for MCFC components are presented in Table 2. During the lifetime operation of MCFC, each of the MCFC components shows performance degradation resulting in increased overpotentials and ohmic resistance, thus reducing the net voltage (or current density) available from the cell. The state of the art MCFC materials and the various causes of degradation of MCFC components are listed in Table 2 [5, 6]. The degradation in MCFC typically proceeds in two stages as shown in Fig. 3:

Linear decay: This type of degradation occurs due to the increase in the ohmic resistance of the cell and polarisation resistance of the electrode, mainly cathode, caused by the loss of carbonate electrolyte due to vaporisation or reaction with cell components.

Accelerated decay: This occurs due to the internal short circuiting caused by Ni shortening phenomenon

(discussed in detail in the following section) and fuel crossover through the matrix.

To compete with conventional power generation systems, a generally agreed target life span for MCFCs is ~40,000 h and the system is allowed to be shut down after this period. To achieve the required lifetime and reduce costs, the MCFC component materials need to be modified or new materials need to be developed. Also investigation on the fundamental understanding of various MCFC electrode processes such as cathodic oxygen reduction, effect of carbonate melt wettability on MCFC materials and mechanisms of corrosion of cell components are critical to achieve this goal. Apart from materials' stability, the cost of the MCFC system needs to be lowered for mass commercialization. At present, the average installed cost for a commercially available MCFC like FCE Inc's DFC 1500 module exceeds $4,000 per kW in which the fuel cell stack module cost is $2,400 per kW with the materials' cost as the major contributor (59 %) as indicated in 'Technology Gap Assessment' by US National Renewable Energy Laboratory [7]. The high costs of MCFC stacks are attributed to relatively lower power densities (~120 mW cm^{-2}) of MCFC systems, and a 20 % improvement in power densities can substantially reduce the cost of power from MCFC. If the installed cost of MCFC can be reduced to $2,000 per kW, it could be a preferred choice for stationary power generators above 400 kW range.

Thus, even though the MCFC technology is already commercialised to some extent, there is always a demand for better and cheaper materials to improve the performance and make MCFC an effective replacement for traditional power generation. Hence R&D is continuing around the world to resolve the outstanding issues, improve the overall performance and lifetime of the system and reduce the present cost of the MCFC system. In this review, the MCFC materials challenges and the R&D trends over the past decade are discussed.
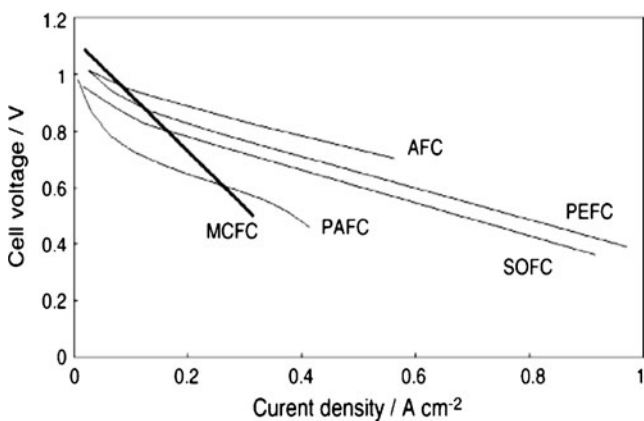
MCFC cathode

General requirements for MCFC cathode materials, besides sufficient electrical conductivity, are limited solubility in carbonate electrolyte at the operating temperature, sufficient porosity (Table 2) to allow the diffusion of reacting species and stability in oxidising atmosphere. At present, lithiated NiO foam is the material of choice for MCFC cathode application. Pure NiO is an n-type semiconductor and the doping with Li^{3+} ion enhances the conductivity by creating extra electron holes for conduction by replacing Ni^{2+} with Ni^{3+}, thus enhancing the electrical conductivity of the cathode. Lithiated NiO also offers better catalytic properties for

Fig. 2 Polarization curve of MCFC compared with those of other types of fuel cells. Figure reprinted from [4] with permission from the publisher

Table 2 The MCFC component materials employed by different developers and associated outstanding issues [2, 5]

Component	Typical material used	Outstanding issues	Approach/solution
Anode	Porous Ni, Ni–Cr, Ni–Al	• Susceptible to creep	• Alloying with other metals
	Pore size 3~6 μm	• Reduction in surface area due to sintering	• Addition of intermetallic phases
	Porosity 50~70 % Sp. area 0.1~1 m^2 g^{-1}	• Insufficient anode wetting by carbonate melt.	• Surface modification and additives such as Ce to enhance the wettability
Cathode	Porous lithiated NiO Pore size 7~12 μm	• Dissolution in electrolyte	Details in Table 3
	Porosity 70–80 % F Sp. area 0.5 m^2 g^{-1}	• Short circuiting across the matrix by metallic Ni	
Matrix	Porous Li–aluminates	• Cracking due to thermal cycling	• Alternative materials
	Pore size 0.2~0.5 μm		• Additives such as alumina
	Porosity 50~60 % Sp. area 0.1~10 m^2 g^{-1}	• Loss of capillary retention of electrolytes	• Matrix reinforcement
Electrolyte	Li–K or Li–Na carbonate eutectic	• Corrosion of cell components • Evaporation	• Rare earth or alkali metal additives to electrolyte
Bipolar plates/ current collectors	Stainless steel SS316, SS310	• Corrosion, Cr dissolution	• Coating or cladding with Ni
			• Additives to MC melt
		• Short-circuiting if conductive corrosion products precipitate	• Corrosion inhibitor coatings
			• Alloying of steel
			• Conductive ceramic coatings

oxygen reduction reaction as compared to bare NiO. Although NiO fulfils the performance requirements such as catalytic activity and electrical conductivity, its dissolution in carbonate electrolyte is one of the issues that limits MCFC lifetime [8–10]. Further, the stainless steel plates are used in the hardware parts like cathode current collectors, and there is a possibility that trivalent species like Fe^{3+} from these materials may become incorporated into the NiO lattice of the cathode and thereby increase the cathode resistance, although this mechanism has been reported to be insignificant in practical operations by some researchers [11].
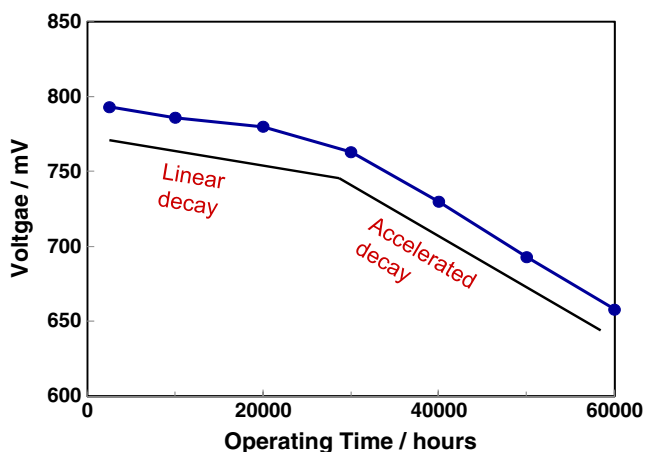
Fig. 3 The stages of progression of voltage degradation over the lifetime of a MCFC based upon data presented in [20]

The dissolution reactions of NiO in molten carbonate are given by:

$$NiO\,(s) \rightarrow Ni^{2+} + O^{2-} \tag{6}$$

$$3O^{2-} + CO_2 \rightarrow CO_3^{2-} \tag{7}$$

Over the past three decades, various researchers have published a number of articles on the studies of the dissolution mechanism of NiO in carbonates and the reduction of the effect thereof [12–15]. Since the dissolution takes place via the formation of Ni^{2+} and O^{2-}, the solubility and the dissolution rate of NiO in a carbonate melt is dependent on the acidic or basic character of the carbonate melt. Depending upon the carbonate melt composition and the molar ratios of the constituent carbonates, the acidic and/or basic type of dissolution behaviour can be observed in MCFCs. For example, in the case of Na_2CO_3/K_2CO_3 mixture, both acidic and basic dissolution mechanisms are identified, while for Li_2CO_3/K_2CO_3 mixture, only a basic type dissolution occurs when the percentage of K_2CO_3 is low (below 50 mol%) in a mixture. Apart from the acid–base character, the rate of dissolution is dependent on temperature and CO_2 partial pressure. In general, higher CO_2 partial pressure in the cathodic chamber and higher temperature lead to higher rate of NiO dissolution. High dissolution rates are a particularly significant problem under pressurised MCFC operation which is desirable for high efficiency. It is particularly

important for practical MCFC operation considering that the pressure of 12 atmospheres would be required on the cathode side to attain a 60 % efficiency based on high heat value in combined heat and power plants with a gas turbine as indicated by Mitsushima et al. [16]. In addition to Ni/Ni^{2+} reduction (Eq. 6) in cathode dissolution, the solid-state phase formation between carbonate melt and NiO ($NaNiO_2$) at lower cell potential is possible at operating temperature of 650 °C as concluded by Belhomme based upon his cyclic voltametric studies carried out on NiO dissolution in Li_2CO_3/Na_2CO_3 [17].

The dissolution of NiO cathode leads to increased cathodic polarisation due to structural changes, possible phase change and Ni shortening. The shortening takes place when Ni^{2+} ions formed in the cathode chamber are transported to the anode and reduced by fuel (hydrogen) to form solid nickel particles. The Ni particles then migrate across the matrix causing the short circuit providing pathways for electron conduction. The rapid degradation in cell voltage occurs due to the internal cell short circuit via percolation of Ni particles. The time taken to short circuit (shortening time) the cell depends upon the thickness of the matrix, partial pressure of CO_2 and the operating temperature of the cell. Various researchers have proposed different empirical correlations to calculate the shortening time [18–20]. In general, the internal shortening time can be expressed as proportional to the inverse of carbon dioxide partial pressure (P_{CO_2}) and to the square of the matrix thickness (L). The general model equation for the estimation of shortening time can be given as: $t_{st} = KL^2/P_{CO_2}$. Yoshikawa et al. suggested an empirical correlation for Ni shortening time as [16, 19]:

$$t_{st} = 6.90 \times 10^6 L^{2.05} P_{CO_2}^{-0.76} e^{\left(54.8 \text{ kJ mol}^{-1}/RT\right)} \quad (8)$$

This correlation is based upon experiments carried out on MCFC with Li_2CO_3/Na_2Co_3 (52:48 mol%) electrolyte and a tape casted γ-$LiAlO_2$ matrix (49 % porosity). The matrix thickness was varied from 0.052 to 0.113 cm and shortening time was determined for various thicknesses. It should be noted that the Ni shortening is a complex process and may vary from system to system depending upon the matrix pore structure and electrolyte melt composition, and hence different researchers have proposed varying values for coefficients and powers in the empirical formula. The instability of Ni particles and the possible particle growth by Ostwald ripening further add to the complexity in determining these values accurately.

As an effect of cathode dissolution, the performance of MCFC, measured as the output voltage at a particular current, degrades over time even before the shortening occurs. Recent results from long-term testing (60,000 h) carried out with a bench-scale MCFC by Morita et al. at Central

Research Institute of Electric Power Industry, Japan indicated that MCFC degradation proceeds in two stages as shown in Fig. 3: the first stage consists of a gradual degradation due to electrolyte loss (increased electrolyte resistance) in the matrix and electrodes, followed by a rapid degradation due to structural changes in the cathode and gas leakage [20]. The time–voltage transient indicated that the decay rate is 4 % (3.3 mV per 1,000 h) of open circuit voltage (OCV) after 10,000 h followed by 8 % (3.5 mV per 1,000 h) after 20,000 h. After 26,500 h, rapid decay in voltage was observed which was attributed to the cathodic overpotential based upon the observation of output voltage of the cell by varying only the cathode gas compositions, keeping other operation variables constant. It is rather interesting that the rapid degradation in voltage occurs even before Ni shortening takes place. From the empirical formulae, the shortening time was estimated to be 31,000 h while actual shortening as indicated by increase in 'short-circuit' current density was observed to onset at 29,000 h under the experimental conditions. Despite the fact that the shortening phenomenon started only after 29,000 h, the performance of the cell decreased rapidly after 26500 h, indicating that the transformation from the gradual degradation phase to rapid degradation takes place because of the increase in cathodic polarisation losses (O^{2-} reduction). Thus, NiO dissolution leading to structural changes or Ni shortening or both contributes significantly to the performance deterioration of MCFC. Thus, while engineering the MCFC cathode and estimating the lifetime, a careful consideration must be given to the increased polarisation before Ni shortening. Various approaches have been taken by the developers and researchers to reduce the dissolution and to arrest the shortening (Table 3). The following are major approaches presently being pursued actively:

1. Use of alternative materials in place of NiO or modification of NiO by doping or coating.
2. Use of additives to molten carbonate electrolyte to increase basic character and suppress the dissolution.
3. Optimising the operating conditions and parameters to minimise the dissolution rate.

Alternatives to NiO as MCFC cathode

Several alternative cathode materials such as $LiFeO_2$, Li_2MnO_3 and $LiCoO_2$ have been investigated to replace NiO [14]. Substantial efforts were carried out by research groups at ECN, Technical University (Netherlands) of Delft, Royal Society of Physics and Argonne National Lab (USA) in the 1990s towards the development of $LiCoO_2$ and $LiFeO_2$ cathodes [21–23].

The major issue with undoped $LiFeO_2$ and Li_2MnO_3 (~0.0014 Scm^{-1} at 650 °C) is low electrical conductivity

Table 3 Various approaches adopted by the MCFC developers to improve the cathode performance

Approach	Materials	Performance*	Ref	Comments/issues
Additives used in NiO cathode	Co 20 mol%	66	[40]	Charge transfer resistance lower than NiO
	Co 1.5 mol%	40	[41]	
	Co_3O_4 nanopowder	10	[43]	
	Ce/Co (9.5 % Co/5 % Ce)	80	[42]	Porosity equivalent of NiO cathodes
	ZnO 2 mol%	94	[44]	Charge transfer resistance higher than NiO
				Dissolution of ZnO in melt
	MgO 8 mol%	13	[16]	Increased cathodic polarisation
	La 0.3 wt%	90	[45]	Lowered charge transfer resistance
	Dy 1 wt%	40	[46]	Requires further electrochemical testing
Coating on NiO cathode	$LiMg_{0.05}Co_{0.95}O_2$ Sol–gel impregnation technique	Stable for 700 h at 100 mA cm^{-2} (0.8 V)	[48]	Conductivity higher than bare NiO cathode
	$LiCoO_2$, electrochemical potentiostatic deposition (Li from carbonate melt)	67	[50]	High charge transfer resistance
	5 % CoO Mechanofusion of Co particles on Ni	90	[51]	–
	$LiCoO_2$ PVA-assisted sol–gel method	50	[52]	Improved voltage efficiency compared to NiO
	Electroplating $LiCoO_2$	84	[55]	Improved voltage efficiency compared to NiO. Stability at higher pressures needs to be evaluated
	LSC Sol gel coating	34	[59]	Higher cathodic overpotential requires optimization in porosity
	$Gd_{0.6}Sr_{0.4}CoO_3$ Vacuum suction	Stable cell performance for 2,200 h at 150 mA cm^{-2} (0.85 V)	[61]	Promising coating material
Carbonate melt modification by additives	$CaCO_3$ 9 mol%	20	[64]	The amount of additives needs to be controlled
	$BaCO_3$ 9 mol%	20	[64]	
	Y_2O_3	25	[64]	The long-term performance under load need to be verified
	Gd_2O_3	10	[64]	
	CeO_2	40	[64]	
	La_2O_3 2 %	90	[65]	
	MgO	78 % reduction in solubility of $Ni_{0.92}Mg_{0.08}O$	[20]	

[a] Percent reduction in NiO solubility or as specified

which is two to three orders of magnitude lower than the lithiated NiO (15 S cm^{-1}) cathode [25]. The electrical conductivity and polarisation resistance of these materials can be reduced by doping with dopants such as Co and Nb. Cobalt-doped $LiFeO_2$ shows a 30-fold enhancement in electrical conductivity and Nb-doped $LiFeO_2$ shows 60-fold enhancement in conductivity; however, only Co-doped $LiFeO_2$ shows a p-type conductivity required for MCFC cathode [26]. Despite the improvement in conductivities, the conductivity of these materials was still lower than NiO, and the overall cathodic overpotential was found to be more than twice that of NiO cathode materials at 650 °C. Furthermore it was found that the electrical conductivity of $LiFeO_2$ cathode is affected by the ratio of Li/Fe which in turn is dependent on the CO_2 partial pressure. At high CO_2 partial pressures (>0.002 atm.), the $LiFeO_2$ phase is 'balanced'

(Li/Fe is 1:1) and resistivity of the cathode is high (300 Ω cm at 650 °C), while at low CO_2 partial pressures, the Li from the carbonate melt reacts with $LiFeO_2$ resulting in a Li-rich phase with resistivity of an order of magnitude lower than the balanced phase (3 Ω cm at 650 °C) [27, 28].

$LiCoO_2$ as MCFC cathode

While $LiFeO_2$ and Li_2MnO_3 attracted limited attention, the other prospective candidate cathode $LiCoO_2$ gained considerable attention and is considered as the most suitable single-phase replacement cathode material because of its relatively lower resistivity (1 Ω cm at 650 °C), low solubility (0.5 μg cm^{-2} h^{-1}, which is an order of magnitude lower than NiO) and faster cathodic kinetics as compared to $LiFeO_3$ [22].

In Fig. 4, the alternative cathode materials are compared with NiO on the basis of cathodic polarisation at various current densities. It is rather interesting that the intrinsic catalytic properties towards oxygen reduction of all three alternative cathode materials are comparable, but it is the better electrical conductivity of NiO-based cathodes that lowers the overall polarisation resistance [29].

A number of synthesis methods are reported for LiCoO$_2$ cathodes for MCFC as well as for other applications such as Li-ion battery electrodes [30]. These methods include sol–gel processing, molten salt synthesis, hydrothermal processes and precipitation routes [25]. It is well known that the synthesis route and starting materials have a pronounced effect on the characteristics of the final electrode. Indeed, the LiCoO$_2$ powders synthesised with different methods have shown considerable variation in particle size, morphology, defect structure and oxygen non-stoichiometry. Hence an opportunity exists for MCFC researchers to develop LiCoO$_2$ cathodes with an engineered microstructure to enhance the electrochemical performance. In such an effort, Lundblad et al. reported the preparation of LiCoO$_2$ cathodes via the thermal decomposition of carbonates followed by tape casting of the powder with micronized pore formers [31]. They sintered anodes in air and argon atmosphere at relatively lower temperatures (700 °C for air and 500 °C for argon) to obtain a fine microstructure. The electrical conductivity (0.31 Scm^{-1}) of the cathodes sintered at lower temperatures was found to be comparable, exceeding the minimum required conductivity of 0.8 Scm^{-1} for MCFC cathode indicating sufficient sintering was achieved. The polarisation studies also revealed the overpotential drop of 57 mV at 160 mA cm^{-2} current density which is a reasonable value for MCFC cathode. However, the contact resistance drop between the current collector and these cathodes

was about 70 mV at 160 mA cm^{-2}, while for the state-of-the art NiO cathode is only 25 mV. The high contact resistance between the current collectors and cathode has been the issue for LiCoO$_2$ cathodes prepared with traditional sintering methods as reported by Bergman [32]. The cathode polarisation overpotentials in excess of 250 mV at 1 A cm^{-2} were observed for LiCoO$_2$, while for NiO cathodes overpotentials were about 100 mV at same current density. The reason behind the increased overpotential was attributed to the formation of a corrosion layer between the current collector (AISI 310) and cathode with a more pronounced effect for LiCoO$_2$. In the case of LiCoO$_2$, the corrosion layer was found to be more porous and comprised of a mixture of iron and cobalt phases, while in case of NiO, it was found to be single phase rich in nickel. In addition to the higher contact resistance, the lower mechanical strength of LiCoO$_2$ as compared to NiO cathodes is also a major issue hindering its use for large area cathodes which is a key requirement for commercial stationary power generators. Furthermore the high cost of cobalt precursors used in the synthesis as compared to Ni can be an issue in commercial development. At the time of writing this manuscript, the price of US $228 per kg was quoted for cobalt nitrate (ACS grade), while for nickel nitrate (ACS grade), it was US $88 per kg, for 5 kg.

LiFeO$_2$–LiCoO$_2$–NiO ternary systems

As the alternative cathodes lack electrochemical performance and practical suitability, the concept of 'composite' or multi-component systems was proposed by Bloom et al. [33]. It was hypothesised that LiFeO$_2$ would reduce the dissolution rate while high conductivity phases such as NiO and LiCoO$_2$ improve the electrochemical performance in such a system. They investigated the phase formation and stability in LiFeO$_2$–LiCoO$_2$–NiO ternary system to improve the conductivity while lowering the dissolution rates. Several compositions with varying molar ratios of constituent oxides were investigated, and it was concluded that for LiFeO$_2$–LiCoO$_2$–NiO ternary system two regions of homogeneity exists in the phase diagram: one rich in LiFeO$_2$–NiO solid solution and other rich in LiCoO$_2$. The lowest resistivity among the ternary system was reported to be 2.6 Ω cm for 75 mol% LiFeO$_2$, 12.5 mol% LiCoO$_2$ and 12.5 mol% NiO. In actual cell tests, the MCFC with these cathodes delivered a voltage of 0.79 V at 160 mA cm^{-2} at 650 °C. No mass transport loss was observed indicating adequate porosity. More recently, Wijaysinghe et al. reported the performance of laboratory-scale MCFCs (3 cm^2) cathodes prepared with 20 mol% LiCoO$_2$ in 25:75 LiFeO$_2$ systems [34]. They prepared starting powders for the cathode via the Pechini process followed by tape casting on a Li-alumina matrix with Li$_2$CO$_3$/K$_2$CO$_3$ electrolytes and standard Ni–Cr alloy anodes. The steady-state polarisation indicated
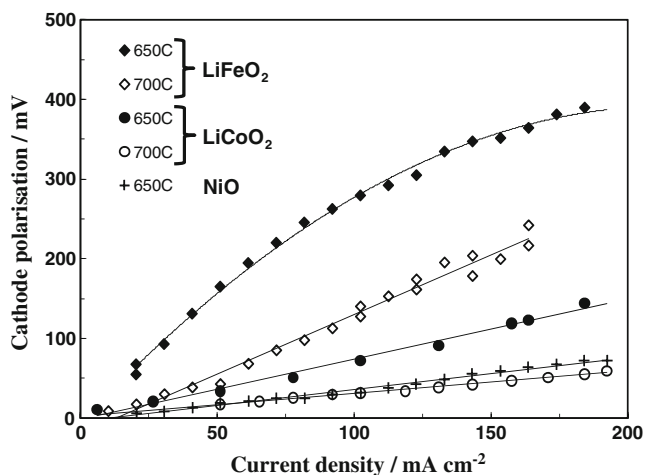
Fig. 4 Comparison of overvoltage losses of alternative cathode materials with NiO cathode. Figure reproduced from [24] by permission of The Electrochemical Society

cathodic polarisation as low as 62 mV at 160 mA cm^{-2} with 80:20 H$_2$/CO$_2$ as a fuel gas at 650 °C. Furthermore, the *iR* drop including the contact resistance was found to be only 46 mV which is nearly the same as for NiO cathodes. Thus, the multi-component cathode systems have shown a promising alternative to conventional NiO, though further investigations on solubility and long-term performance are required. Wijaysinghe et al. also reported the effect of synthesis methods on the fabrication and performance of ternary cathode materials [35, 36]. According to their investigation, the Pechini process seems an appropriate method for preparing starting powders as compared to glycine nitrate route, as the glycine route yields sponge-like structure leading to difficulty in cathode fabrication. Furthermore it was reported that the sintering temperatures higher than 1,000 °C may lead to evaporation of Li in porous cathodes resulting in formation of CoO$_2$ and Fe$_2$O$_3$ in these systems which is detrimental to cathode performance. Based upon their studies on trade-off between porosity, stability and conductivity, the sintering temperatures in between 800 and 900 °C were recommended for ternary cathodes with micron-size graphite pore formers.

NiO modification

NiO cathodes modified by addition of oxides

MCFC cathode stability can also be improved by the addition of additives such as oxides of transition metals, rare earths, etc. to NiO powder. The additives can be added to NiO source powder with traditional approaches such as ball milling, shear mixing or adding cation source compounds such as nitrates. The milled mixture can be subsequently tape casted and sintered on an electrolyte tile as in typical MCFC fabrication methods. During heat treatment, the additives may react with NiO to form a solid solution or intermediate phases or may remain as a separate phase sintered to NiO particles. The enhanced stability of such cathodes is typically attributed to preferential dissolution of additives and/or improved ability to incorporate Li from the carbonate melt; however, more studies are required to understand the detailed mechanism by which additives improve stability.

Cathode stabilisation with cobalt Cobalt is considered as one of the promising additives for NiO cathodes and is widely studied by MCFC researchers. Zecheva and Stoyanova reported in the early 1990s that substitution of a small amount of cobalt in lithiated Ni increases the degree of lithiation (lithium incorporation) which in turn increases the amount of Ni^{3+} [37]. The increased valance on Ni^{3+} bonds better with O^{2-} in the lattice as compared to Ni^{2+}, thus improving the stability of the material. Enhanced lithiation not only improves the stability but also decreases the

charge transfer resistance up to orders of magnitude as reported by Escudero et al. [38]. In Li-ion battery cathodes also, it was observed that the addition of Co improve the electrochemical properties of the electrodes significantly [39].

For MCFC application, Ganesan et al. reported the characterization of a cathode with 20 mol% Co-doped lithiated NiO (LiNi$_{0.8}$Co$_{0.2}$O$_2$) prepared via a non-aqueous tape casting of oxide powders synthesised by traditional solid-state reaction [40]. In the solubility tests under typical MCFC conditions, the atomic absorption spectroscopy revealed 9 ppm mol fraction of nickel in carbonate melt for modified cathode and 27 ppm nickel for undoped cathode after 100 h. However, a cathodic polarisation of about 95 mV was observed for a doped cathode as compared to only 55 mV for an undoped NiO. The electrochemical impedance spectroscopy (EIS) measurements under varied cathodic gas conditions indicated that the fundamental mechanism of oxygen reduction is similar to NiO cathode and the cathodic charge transfer reaction follows a positive order for O$_2$ concentration and a negative reduction order for CO$_2$ as in case of NiO. The higher polarisation resistance was attributed to decreased porosity in Co-doped NiO cathodes (38.5 %) as compared to bare NiO (50–55 %). Thus, it is evident that while selecting the additives for MCFC cathodes, it is critical to understand the effect of additives not only on dissolution and intrinsic electrochemical properties, but also on the microstructure of the cathodes as the phenomenon such as reduction in porosity or change in pore structure would obviously has a pronounced effect on MCFC cathode performance. One of the approaches is to use the lower amounts (1 to 10 %) of additives to avoid any significant change in microstructure. Senung-Goo Kim reported the performance of 1.5 % CoO and 1.5 % LiCoO$_2$ prepared by mixing nitrates of respective metal with NiO followed by tape casting [41]. The cells with modified cathodes demonstrated power densities of 125 mW cm^{-2} after 1,000 h of operation. Although the power density was found to be slightly less than bare NiO (129 mW cm^{-2}) cathodes, the amount of precipitated Ni in carbonate melt was 40 % less in the case of doped cathodes after 1,000 h of operation.

The cathodes made with NiO particles coated with oxides (core–shell structure) or with oxides finely dispersed on NiO particles have been evaluated in recent years. Kim et al. reported synthesis and characterization of cathodes with finely dispersed Ce/Co on NiO particles prepared via polymeric precursor using the Pechini process [42]. The sintered cathodes were shown to retain the microstructure similar to traditional NiO cathode with pore size of 6–10 μm and up to 80 % porosity for 10 mol% Ce/Co (9.5 mol% Co and 5 mol% Ce)-doped composition. Based upon 350 h of testing, the dissolution of these cathodes (5.54 ppm) was lowered to 80 % of the pure NiO (30.35 ppm) at 650 °C
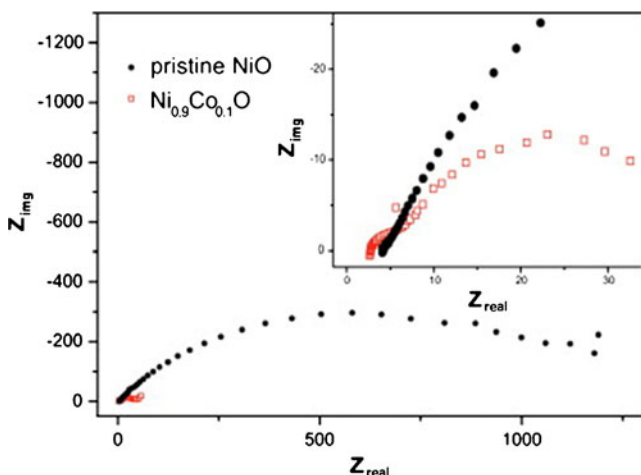
Fig. 5 Effect of addition of cobalt nanoparticles on NiO cathode polarisation, as shown by the impedance spectrum. Figure reprinted from [43] with permission from the publisher

under standard cathode conditions. Since the manufacturing process is potentially scalable, this approach appears promising for trials in commercial settings. Recently Kim et al. reported the effect of cobalt nanoparticle addition on the dissolution of NiO [43]. They reported that NiO cathodes mixed with Co_3O_4 nanopowder (10 mol%) results in in situ formation of solid solution resulting in $Ni_{0.9}Co_{0.1}O$ formation, which showed an order of magnitude lower charge transfer resistance at 650 °C under (0.66/0.33 CO_2/O_2) atmosphere (Fig. 5). The improved charge transfer resistance was attributed to enhanced lithiation as the neutron diffraction studies on cathodes after 100 h of testing revealed that the concentration of Li was 3.4 mol% in these cathodes as compared to 2 mol% for NiO. The cathode particles showed a core–shell-type structure with lithium concentration decreasing from the surface to the core. The dissolution of these cathodes was reported to be 8.3 ppm which is significantly lower as compared to NiO (30.3 ppm) after 300 h at 650 °C under (0.66/0.33 CO_2/O_2) atmosphere in $(Li_{0.62}K_{0.38})_2CO_3$ melt.

Cathode stabilisation with other oxides Besides Co, a number of other metal oxides such as ZnO, MgO, FeO_3 and a number of lanthanides have been investigated as additives. B. Huang et al. reported the effect of 2 to 10 mol% addition of ZnO on NiO stability [44]. The solubility tests at 65 °C under 0.67 atm. CO_2/0.33 atm. O_2 atmospheres indicated that even with 2 mol% addition of ZnO the cathode solubility decreases to 2.32 mol ppm (Ni^{2+}) from 35 mol ppm for bare NiO cathode for 200 h. The reason behind the lower solubility was attributed to preferential dissolution of ZnO to increase O^{2-} concentration in the melt which pushes the equilibrium in Eq. 6 to the left hand side as per le Chatelier's principle. This hypothesis was confirmed from XRD which

revealed that the peak for ZnO had completely vanished after 200 h even with 20 mol% addition of ZnO to the cathodes. As ZnO content increases, the dissolution rate of Ni decreases only slightly but charge transfer resistance increases by an order of magnitude from 275 Ω (2 wt% ZnO) to 1,906 Ω (6 wt% ZnO). Escudero et al. reported the effect of 0.3 to 0.8 % lanthanum additions on MCFC cathodes [45]. They also reported the best electrochemical performance and the highest degree of lithiation with 0.3 wt% La as compared to 0.5 wt% La. Similar results have been reported for Dy-doped NiO cathodes by Liu et al. [46]. Only 1 wt% of Dy effectively reduces the dissolution of 19.4 to 11.8 ppm. The improved performance was attributed to enhanced lithiation and increased basicity of the melt by preferential dissolution of Dy. It is not however clear why the dissolution rate and performance varies significantly with only a little variation in the amount of additives. For practical applications, the addition of a rare earth such as Dy in low amounts can be an option considering the recent decrease in the price of Dy; however, more studies in actual cells for longer durations are required. Hunag et al. reported the EIS studies and solubility studies on 0.3, 0.6 and 1 wt% yttria-added NiO [47]. They observed that the addition of yttria not only promotes the charge transfer reaction as shown in Fig. 6, but also lowers the dissolution rates of Ni, from 35 mol ppm (NiO cathode) to 1.65 mol ppm (with 0.3 wt% yttria). Further it was reported that the variation in charge transfer resistance and double layer capacitance (which is related to interfacial area) in the samples containing yttria stabilises after 200 h. While it is evident from recent MCFC literature, the enhanced lithiation and preferential
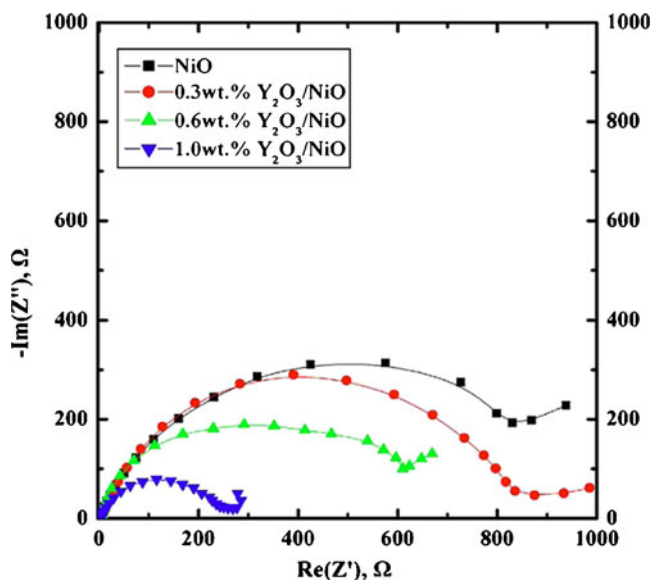

Fig. 6 Effect of addition of yttrium oxide nanoparticles on NiO cathode polarisation, as shown by the impedance spectrum. Figure reprinted from [47] with permission from the publisher

dissolution of additives in the carbonate melt contributes to the improvement in stability of cathodes. However, the EIS obtained in these reports are under OCV conditions and studies are required to find out stability under load conditions. Also the details on the spatial dimension of the additive-rich layer in the carbonate melt and its stability under high cathodic current densities need to be investigated. It is well known that high current densities significantly alter the ceramic electrode's performance as well as the structure and interfacial dynamics.

NiO cathodes modified by protective coatings

LiCoO₂ as a cathode coating The modification with coating layer of protective oxide approach involves fabrication of NiO typically by tape casting and using a porous tile as the skeleton. A number of different methods can be used for coating, such as wet impregnation, dip coating, sol–gel methods, electrophoretic depositions, potentiostatic electrolysis depositions, chemical vapour deposition and laser ablation. The spinel materials LiFeO₂ and LiCoO₂ are obvious choices as coating material. Since LiFeO₂ has low conductivity, LiCoO₂ has been studied extensively as a coating material using a number of different coating methods [48–52]. In all cases, the cathode stability improved significantly as indicated by decreases in solubility in carbonate melts by about an order of magnitude. Brenscheidt et al. have shown that 40,000 h of operation can be achieved with a 95-μm LiCoO₂ coating on porous NiO support [53]. Further, the process such as sol–gel dip coating could be relatively simple and cost effective for practical applications. A typical example of such a process is shown in Fig. 7. In recent work at ENEA laboratories, the NiO cathode was coated with LiCoO₂ via a complex sol–gel process [54]. After coating the Fe–MgO-doped NiO cathode with the precursor, the cobaltite film was formed in situ in a MCFC. The coated cathodes demonstrated improved stability and comparable polarisation resistance with NiO cathodes. While the results indicate the potential of the method for making it applicable for practical applications, the various factors such as cations to fuel ratio, the complexing agent and gelation type need to be comprehensively studied. Furthermore the physical characteristics of the coated film such as thickness and effect of coating on microstructure need to be carefully adjusted as the polarisation resistance of the cathode could increase significantly with the reduction in porosity. One of the other issues in coating process involves the fabrication of the coated matrix, and dipping in the solution baths would be in the handling of the fragile large area matrix in commercial environments. The methods as such use coated particles for tape casting, or in situ formation of the protective layer could be a better alternative as it avoids the additional processing step (dipping).
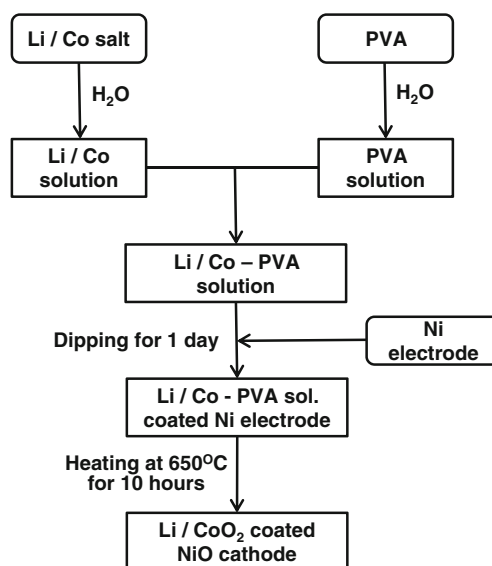

Fig. 7 Flow diagram of typical PVA-assisted sol–gel coating process for NiO cathode. Figure redrawn from [52]

In addition to the chemical routes, the electrochemical coating processes such as electroplating or potentiostatic deposition can be used to coat the cathodes in situ or ex situ. The electrochemical performance of MCFC with in situ deposition of LiCoO₂ on NiO cathode by electroplating was studied by Kuk et al. [55]. They reported formation of hcp-structured LiCoO₂ spinel on the cathode of MCFC and the cell delivered the power density of 120 at 150 mA cm^{-2} for 300 h of operation. The fundamental studies on correlation between the exact nature of the films formed in terms of oxidation states; crystal structure and thickness; and processing parameters such pH, deposition voltage/current, etc., are scarce in open literature. Mendoza et al. presented a study on the potentiostatic deposition of CoO on Ni foil and on rotating disc electrodes [56]. They concluded that a previously oxidised NiO provides better adherence when coated at a lower applied oxidation potential of 0.50 V with a pH of salt bath at about 7.4. Higher oxidation potentials (>0.50 V) lead to agglomeration of deposited particles and poor adherence. Furthermore, they concluded that irrespective of processing conditions, the Co₃O₄ is formed after deposition and it changes to CoO after annealing at 700 °C. After the cobalt oxide coating is formed, its lithiation can be done in situ in MCFC. Typically, in the presence of molten carbonate, lithiation of cobalt oxide films takes place within a few minutes [57]. As is the case in chemical processes, the electrochemical processes can be modified with chelating agents or stabilisers to obtain a higher deposition rate or better quality coating. However, these additives must be carefully chosen to suit the deposition process. Mansour et al. reported a study on the effect of complexing agent in the coating of a MCFC cathode using the

potentiostatic process [58]. They concluded that glycine used in higher concentrations has a negative effect on the coating rate and adherence. Hence, the use of the complexing agents such as citrates or tartrates is recommended in the electrochemical deposition process instead of glycine.

Other coatings In addition to LiCoO2, other coatings such as lanthanum strontium cobaltite (LSC) have been investigated [59]. The solubility of the NiO cathode was reduced from 30 to 20 mol ppm after 100 h of testing; however, cathodic polarisation increased almost two times (109 mV) from 59 mV for the uncoated NiO. At higher current densities above 150 mA cm^{-2}, a significant mass transport loss was observed indicating reduction in porosity due to the coating.

The reduction in porosity as a consequence of the coating may be compensated with highly active electrocatalyst coatings such as ceria. Soler et al. reported the performance of MCFC with Ce nitrate-impregnated cathodes [60]. The cells with modified cathodes delivered improved performance (150 mW cm^{-2}) as compared to NiO cathodes (about 112 mW cm^{-2}) for more than 2,200 h of testing period. Although the porosity of cathode was reduced by 5 %, the performance was actually improved, possibly because of electrocatalytic activity and oxygen storage capacity of ceria. The post-mortem analysis of the cell with SEM-EDX showed scarce deposition of 'loose' nickel on ceria-coated cathode while a significant amount of Ni was detected for the traditional NiO cathode. Recently, Song et al. reported electrochemical performance of a gadolinium strontium cobaltite (GSC: Gd$_{0.6}$Sr$_{0.4}$CoO$_3$)-coated cathode prepared by vacuum suction of a solid GSC slurry on a NiO plate [61]. The coating lowered the charge transfer resistance with faster oxygen reduction reaction at the cathode, thus reducing the activation energy of the cathodic charge transfer from 83.5 to 53.6 kJ mol^{-1}. The cell delivered stable power densities of about 127 mW cm^{-2} at 150 mA cm^{-2} during 2,200 h of testing with peak power density of 210 mW cm^{-2} at 300 mA cm^{-2} as shown in Fig. 8. The fast peroxide mechanism was claimed at a lower temperature of 600 °C which is typically observed only at a higher temperature (700 °C) with NiO cathodes. Thus, the performance and stability of coated cathodes appear promising and it opens up the possibility of exploring various oxides and electrocatalysts such as perovskites as coatings in MCFC cathodes for further enhancement in performance and stability. The issues such as coating adherence, coating continuity and reduction in porosity need more detailed studies. Considering the MCFC setup and corrosive atmosphere, these types of studies remain a challenge especially for in situ-treated cathodes.
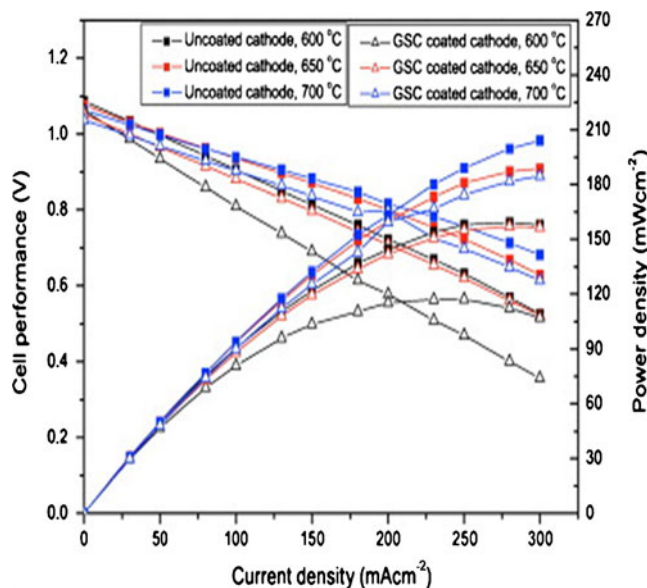

Fig. 8 I–V–P curves of MCFC with NiO cathode coated with gadolinium strontium cobaltite (*GSC*). Figure reprinted from [61] with permission from the publisher

Modification of carbonate melt

The electrolyte modification by changing the basicity of the electrolyte mixture by the addition of rare earth additives to the carbonate melt is another way to reduce NiO dissolution. The oxides of various alkali, alkaline and rare earth elements can be added directly to the carbonate melt to the amount such that the electrochemical performance of the electrolyte material is not deteriorated. Since the early 1990s, it was observed that the addition of additives such as CaCO$_3$, SrCO$_3$, etc. reduces the solubility of NiO up to 50 % in the carbonate melt [62]. Tanimoto demonstrated that the MCFC lifetime can be improved by 15–20 % even under accelerated degradation conditions (0.58 MPa pressure and 85 % CO$_2$–O$_2$ mixture on the cathode side) with addition of 9 mol% Ca or Ba carbonate to Li/Na carbonate without affecting the performance [63]. Morita et al. reported that the addition of La to Li/Na electrolyte results in up to one tenth reduction in solubility of NiO [20]. Based upon the calculated shortening time, it can be deduced that the cell with La additives can deliver 40,000 h under high-pressure operation as shown in Fig. 9. This is particularly interesting since high pressure leads to more efficient MCFC operation. The improvement in solubility resistance can be explained by the formation of phases between the additive and carbonate like oxycarbonates such as La$_2$O$_2$CO$_3$. These complexes are highly soluble in carbonate melts and tend to increase the basicity of the melt. This, in turn, decreases the solubility of the NiO. Matsuzawa et al. proposed that electrostatic characteristics of the cation and melt can be used to select the right cation for the carbonate melt [64].
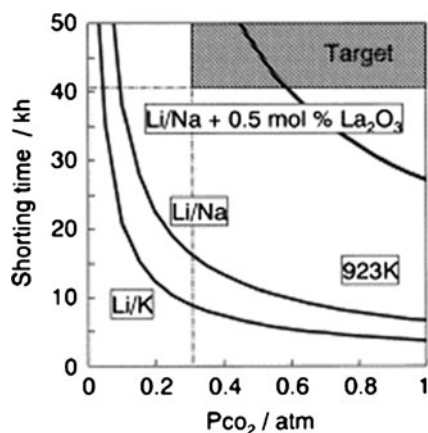
Fig. 9 Effect of La addition to carbonate melt on Ni shortening time. Figure reprinted from [16] with permission from the publisher

Based upon the coulombic forces between the molten species, they have defined a parameter $\acute{\varepsilon}$, which is useful to roughly estimate the solubility of NiO in carbonate melt with different oxides added. The parameter $\acute{\varepsilon}$ is expressed as:

$$\acute{\varepsilon} = \frac{1}{N_c} \sum_{i_c}^{N_c} \frac{Z_c^2}{r_c}$$

Where, N_c = number of cations, Z_c = valance number and r_c is the radius of the cation. Supported by the experimental results, they found that to decrease the NiO solubility, a smaller radius and higher valence cation (with a large solubility in carbonate melt) would be effective as an additive to the electrolyte matrix. This is evident from the fact that La which has higher value of parameter $\acute{\varepsilon}$, when added to carbonate melt, decreases the solubility of NiO to a minimal value in comparison with other additives [65]. For the tested additives (La, Y, Ca, Ba, etc.) the linear correlation between $\acute{\varepsilon}$ and solubility of NiO in carbonate melt is observed on a log–log plot. In other words, the higher the parameter $\acute{\varepsilon}$ for a given additive, more stable would be the cathode. The work suggests a 2 wt% addition of lanthanum to be more effective than alkaline earth metal carbonates as well as other rare earth additives. The additives including lanthanum not only reduces the dissolution but also enhances the oxygen dissolution, perhaps the electrocatalytic activity and thus potentially improves the kinetic performance of the cathode [66, 67]. It has been observed that with addition of 0.5 wt% CeO_2 and 0.5 wt% La_2O_3, the charge transfer resistance in Li/K melt decreases by an order of magnitude. As the charge transfer resistance in MCFC is governed by oxygen partial pressure, the enhancement of electrochemical performance can be attributed to the reduction of CO_2 partial pressure near the cathode due to the increased oxygen because of donation in case of CeO_2 and carbon dioxide capture in the case of La_2O_3 additives.

Control of NiO dissolution by adjusting MCFC operating conditions

In addition to the cathode materials modification, it is also possible to decrease the cathode dissolution by controlling operating parameters such as gas composition and operating temperature. In recent work, researchers at Ansaldo Fuel Cells showed that the cathode polarisation can be reduced by adopting a cathode gas devoid of non-reacting species: nitrogen [68]. Two tests were carried out on identical cells: one with a mixture of air (70 %) and CO_2 (30 %) and the other with a mixture of pure O_2 (33 %) and CO_2 (67 %). The cathodic polarisation of cell tested with air was found to be considerably higher. The presence of inert gas (N_2 in air) was believed to affect the diffusion process in the molten carbonate film on the cathode and thus an increase in the cathodic polarisation under high current densities was observed. It should be noted that for practical operation the conditions optimised for the cathode may be detrimental for the stability of other components such as the anode and the matrix. The cost of pure oxygen would be another issue.

Apart from the above-discussed approaches for the minimization of the cathode dissolution, Bergaglio et al. of Ansaldo Fuel Cells proposed an alternative strategy which involves matrix modification by coating and keeping the NiO cathode unaltered. In a multilayer gamma lithium aluminate matrix, one layer on the cathode side was replaced by a lithium ferrite layer to form a 'cathode–ferrite–matrix' sandwich. The anode material used was standard Ni–Cr anode. The operation up to 3,750 h was reported with maximum power densities ranging from 1.53 to 1.85 kW m^{-2} without observing a significant dissolution [69]. The cells were operated at atmospheric pressure with fuel gas (H_2/CO_2=90:10) and the oxidant gas (air/CO_2=70:30). Also, the cells were reported to cope with thermal cycling when subjected to two planned shutdowns and restarts during the operation. Further investigations on the scale-up of the concept and stability are reported to be in progress.

In addition to arresting the cathode dissolution problem, the development of cathodes to improve power densities would be beneficial to achieve the cost targets for MCFCs. By optimising the pore structure and porosity to increase the electrochemically active sites, the power densities can be improved to some extent. At this stage, the average power densities of commercial MCFC systems (0.12 to 0.15 W cm^{-2}) are considerably lower than the SOFC systems (0.25 Wcm^{-2}) [70]. Selman indicated that if the areas of reactive sites inside the MCFC electrode can be matched with fuel cells such as phosphoric acid and polymer membrane fuel cells, the high power density in order of 0.5 W cm^{-2} is achievable in state-of-the art MCFC systems [71]. This suggests a 20-fold increase in the surface area of the cathode (and anode), which is obliviously not achievable for

MCFC cathodes, but it is clear that any improvement in surface areas while maintaining the electrical conductivity of electrodes would increase the power density.

MCFC anode

The MCFC anode is also a porous structure like the cathode which allows diffusion of gases and collects current from triple-phase boundary interfaces at reaction sites. General materials required for MCFC anode have good electrical conductivity and structural stability and suitable catalytic properties for the type of fuel used. Since the reaction kinetics (oxidation of fuel) is faster at anode side of MCFC at the operating temperature, the base metal catalysis (Ni) is sufficient for hydrogen fuel. Therefore less surface area is acceptable in case of the anode as compared to the cathode as indicated in Table 2. Since the early stages of development of MCFC, the pure Ni-based anodes have demonstrated reasonable electrochemical performance with polarisation losses less than 30 mV at 160 mA cm^{-2} [72]. These anodes can be manufactured using well-established powder metallurgy techniques such as hot pressing or tape casting of metallic powders. One of the issues with the pure Ni anode is performance degradation and shrinkage due to creep and sintering. Furthermore the manufacturing processes and typical operating conditions of MCFC lead to compressive stress at high temperatures on MCFC components including the anode. These conditions are clearly favourable for the creep-type failures of metallic components in MCFC. The high creep strains (40 %) have been observed in the case of pure Ni anodes within the first 100 h of operation [73]. The creep exponents of pure Ni anode are close to the Nabarro–Hearing-type creep (diffusion of vacancies within crystal lattice) or Cobel-type creep (diffusion of vacancies via grain boundaries) [74]. Apart from the creep, the decrease in the surface area and shrinkage due to sintering (via neck formation-mass transport) cause the degradation in performance of anodes during the initial few days of MCFC operation. To overcome these problems, alloying of Ni anode with various metals such as Cr, Al and Cu is a common approach taken by the developers [75–77]. The Ni alloyed with Al or Cr is considered stable and possesses sufficient electrochemical activity for MCFCs operating on H$_2$ fuel [78]. Hence compared to the cathode, not many literature reports are available on MCFC anode stability; nonetheless, few research groups have continued the efforts to improve the stability of the anode and improve the creep resistance to improve the performance further. Arresting the creep by addition of intermetallics is a well-proven technique used in high-temperature metals engineering. Wee et al. studied the effect of addition of intermetallic powders (Ni$_3$Al) on the sintering and creep resistance of the NiO

anodes [79]. They found that the addition of 5 wt% Ni$_3$Al phase along with 3 wt% Al decreases the shrinkage and also prevents the porosity collapse. The studies by Kim et al. showed that the addition of Ni$_3$Al increases the sintering resistance by arresting the grain boundary movements and subsequently impeding the mass transport [76]. Apart from the creep, the resistance to corrosion is important in a reducing atmosphere in anode chamber. The lanthanides such as Dy came up as promising additives to anodes as in case of cathodes. Addition of 5 wt% Dy reduces the corrosion rate by an order of magnitude with the formation of a Dy intermetallic phase (Dy$_2$Ni$_{17}$) [80].

As in the case of cathodes, an improvement in the electrochemical performance of the anode is desired. As MCFC operation relies on the ionic exchange between the melt and solid electrodes, the wetting of the electrodes (the wetting angle) especially on the anode side is an important parameter determining the MCFC performance. The wetting angle for standard MCFC anodic gas composition is around 50° with (Li/Na)$_2$CO$_3$ and 31° (Li/K)$_2$CO$_3$ [81]. Hence efforts are being made to improve the wetting of the anode using the coatings or additives. Hong et al. received a US patent which describes the method of coating the Ni anode with Al and Ce via slurry dip coating [82]. They demonstrated that with addition of 4 wt% Al, the wettability of the anode improves from about 14.1 to above 40 %. As a result, the maximum current density obtained from a single MCFC unit increased from about 100 mA cm^{-2} (at 0.58 V) to about 150 mA cm^{-2} (at 0.8 V) with stable performance during a 500-h testing period. Wee has reported the effect of Ce addition (1 to 5 %) on the performance of Ni–Cr alloy anode [83, 84]. While the addition of Ce improved the contact angles compared to bare Ni–Cr anode, the wetting angle decreased from about 84° for 1 wt% Ce sample to 74.5° for 5 wt% Ce sample. Furthermore, it was reported that the stability of anodes with 3 wt% Ce is at maximum as concluded by testing the cell for 200 h. Thus, the amount of additives need to be optimised to maximise the performance. Also, the addition of less conductive additives such as Ce would increase the ohmic resistance of the anode, and its addition can impede conducting path even if used in relatively smaller amounts. Apart from the material composition and morphology, the electrolyte melt distribution and amount in the anode pores are important characteristics that determine the performance of the anode. For Ni–Cr anode 5–25 % electrolyte fill demonstrates the maximum performance with Li/Na carbonate melt as an electrolyte [85]. However, some researchers have investigated the use of anodes as an electrolyte reservoir to compensate for the electrolyte loss from the matrix during long-term operation of MCFC. Youn et al. reported on the use of Ni–10 wt% Cr anode as an electrolyte reservoir [86]. The anode was coated with boehmite(γ-AlO(OH)) sol via a dip coating process

which was then converted into Li-aluminate particles in situ during the cell operation. The surface modifications allowed an increase in the electrolyte filling of anode to 50–60 vol%. The coating resulted in good electrolyte wettability as compared to the bare Ni surface which partially compensates for the decrease in conductivity by providing additional sites for reaction. The polarisation characteristics of a coated cell with additional electrolyte were found to be slightly inferior to a standard cell (25 vol% electrolyte), but the results suggest that the surface modification could be used to modify the anode surface to make it function as an electrolyte reservoir.

Fuel reforming catalysts and anode modifications in MCFC

As MCFC systems are considered mainly for stationary power generation, significant efforts have been made over the past few decades to develop MCFC systems fuelled with 'real world fuels' such as natural gas, digester gas and allied hydrocarbon fuels. These fuels can be reformed to H_2 and CO inside the MCFC unit or externally using a separate reformer. The reforming reaction is [87, 88]:

$$CH_4 + H_2O \rightarrow CO + 3H_2, \ \Delta H_{923K} = 206 \text{ kJ mol}^{-1} \quad (9)$$

The CO generated can be further reformed into H_2 via the water gas shift reaction.

$$CO + H_2O \rightarrow H_2 + CO_2, \ \Delta H_{923K} = 41.1 \text{ kJ mol}^{-1} \quad (10)$$

Since heat from the electrochemical oxidation of fuels and steam form can be utilised for reforming inside the anode chamber, the MCFCs with direct in situ reforming (DIR) are more efficient than those with external reforming. In a high-temperature fuel cell like SOFC operating at temperatures from 800 to 900 °C, the reforming can be achieved using the Ni–YSZ anode itself as a catalyst. In the case of MCFC, DIR is achieved by placing the reforming catalysts into the fuel channels as the catalytic activity of the conventional MCFC anode is not sufficient for reforming because of the lower surface area and lower operating temperature of MCFC as compared to SOFC [88]. Figure 10 shows a schematic of a DIR catalysis arrangement in MCFC. The placing of the catalyst in fuel channels can be accommodated by modification of cell hardware. Typically, supported metal type catalysts are used for internal reforming. Commercial suppliers of MCFC systems (such as FCE, Mitsubishi) and research organisations (CNR-TAE Institute) developing MCFCs have tested DIR MCFCs with catalysts such as NiO/MgO, NiO/alumina and Ru/ZrO$_2$ and have reported the following issues with DIR catalysts [89, 90]:

1. Deactivation of catalysts due to carbonate electrolyte. The carbonate electrolyte can reach the catalyst in two ways: transport across the metallic fuel channel walls
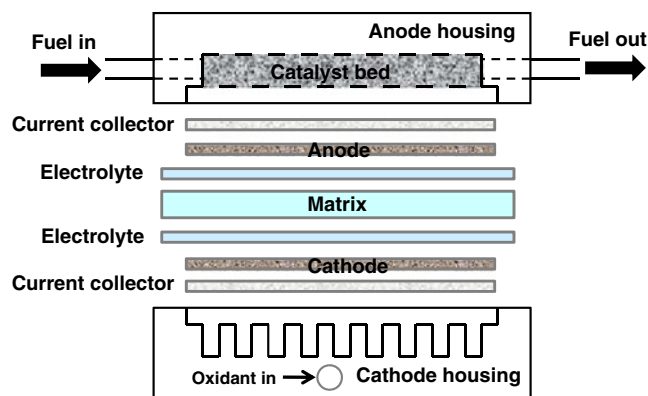

Fig. 10 Schematic of DIR catalysis arrangement in MCFC. Figure redrawn from [80]

(or creep) and/or the vapour phase transport via formation of alkali metal hydroxides such as LiOH or KOH because of the steam generated in the anodic environments. Berger et al. investigated the mechanism of alkali transport towards the catalysts in detail [91]. They concluded that vapour phase transport is the main transport route in case of DIR in fuel channels. It was also found that it is primarily due to Li in the electrolyte melt which migrates on active catalysts sites as reported by Moon et al. [92].

2. Sintering of support and catalyst. The sintering phenomenon typically results in the reduction of surface area of the support and an increase in the particle size of the catalyst due to sintering.

3. Catalyst poisoning in the presence of sulphur as sulphur is readily chemisorbed on the Ni surface to occupy the reactive site. The reaction of sulphur with Ni results in the formation of NiS which is detrimental for electrical conductivity.

4. Carbon decomposition (or coking) during hydrocarbon cracking especially with heavier hydrocarbons similar to that observed in SOFC systems. The coking phenomenon is associated with CO Boudouard reaction which is thermodynamically favoured below 700 °C and with thermal cracking [93].

5. The development of heat gradient in the cell due to fast reforming on the inlet side and no reforming on the exhaust side.

Figure 11 shows the typical degradation of Ni/Al$_2$O$_3$ supported catalyst over the period of 1,000 h. The Ni/MgO–Al$_2$O$_3$ is considered as the best catalyst in terms of alkali resistance, but up to 60 % degradation in catalytic activity may occur in these catalysts as reported by Matsumura et al. of Mitsubishi Corporation [94]. The similar degradation trends can be observed for other catalysts as well. Thus, a significant opportunity exists in R&D on
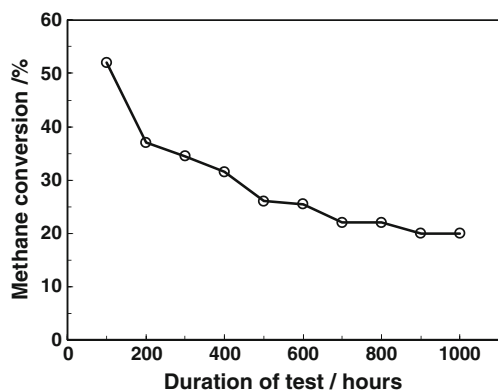
Fig. 11 Degradation of commercial nickel/calcium aluminate high temperature steam reforming catalyst over the lifetime of the MCFC. Figure redrawn from [88]

system designs as well as catalysts in DIR MCFCs. A number of reports have been published on the development of alternative catalyst materials such as Ni–TiO-doped MgO; MgO, CaO, SrO and CeO$_2$ addition to Ni–YSZ Rh/Ru on YSZ; etc. [88, 89, 95–97].

Phase formation between the support and catalysts is a common phenomenon observed in high-temperature catalysts such as reforming catalysts or three-way catalysts. Such phase formation can be avoided with the use of mixed phase supports such as Mg–TiO. In such systems, the ratio of constituent elements (e.g. Mg/Ti) has a significant effect on the stability of the catalysts. Choi et al. reported the stability of Ni catalysts with MgO–TiO$_2$ support with Mg/Ti molar ratios 2, 1 and 0.5 against Li$_2$CO$_3$ attack [98]. When catalysts were not exposed to Li$_2$CO$_3$, the effect of molar ratio was insignificant, but with the exposure to Li$_2$CO$_3$, Ni–MgO catalysts lost all catalytic activity. The deactivation of the catalyst was due to the formation of ternary solid solution of Ni–Mg–Li leading to the loss of active sites on the Ni surface. The titania-doped supports were found to be more stable when the molar ratio of Mg/Ti is 2:1 (Mg$_2$TiO$_2$) with only 2.5 % reduction in catalytic activity for reformation of methane. Park et al. reported the alumina-doped MgO with Mg/Al ratio 2:1 (Mg$_2$AlO$_3$ phase) [99]. The catalysts demonstrated constant catalytic activity for 300 min testing with CH$_4$ fuel even after poisoning with lithium (5.7 wt%) and sodium (6.5 wt%). Earlier, Shin et al. investigated the effect of rare earth doping on the activity of Ni/MgO catalysts [100]. It was observed that up to 10 wt% Gd$_2$O$_3$ can be added to the catalysts resulting in improved coking resistance and enhanced dispersion of Ni on the support. The traditional precious group metal catalysts obviously (Ru–Rh) show improved conversion and stability, but because of the high cost of these catalysts, the commercial developers kept the development focus on NiO-based catalysts. The FEC Inc claimed that the 'DIR-5' catalyst developed by them offers five times more stability

than conventional catalysts and the direct fuel cell technology has demonstrated this for both natural gas and diesel fuels. Besides traditional supported catalysts, zeolite-based catalysts are being studied recently. Zhang et al. reported preparation of core–shell-type catalysts with Ni/Al$_2$O$_3$ core coated with about 3.5 μm thick layer of Sil-1 zeolite layer [101]. As shown in Fig. 12, a zeolite-coated catalyst showed better performance as compared to Ni/Al$_2$O$_3$ but the conversion activity dropped below 40 % within 100 h of operation when exposed to Li/K electrolyte vapours. More studies are required to demonstrate suitability to the use of such catalysts in commercial systems.

Apart from internal reforming catalysts, the anode itself needs to be tolerant of impurities such as sulphur and carbon. To make the anodes more tolerant towards the impurities, the anode materials have been modified by coating with additives or catalysts. Fang et al. reported the surface alloying of NiO anode with niobium using a molten fluoride process [102]. The surface alloying demonstrated significantly lower corrosion rate (0.02 mm per year compared to 0.17 mm per year for bare NiO) in a carbonate bath and improved electrocatalytic activity towards CO oxidation. The lower solubility is attributed to the formation of a composite phase NiO, Nb$_2$O$_3$, and the improvement in electrocatalytic activity was mainly due to the improvement in the wetting angle and increased surface area after the surface treatment. Devianto et al. reported sulphur-resistant anodes synthesised by dip coating NiO in a Ce precursor followed by calcination to get a 2 wt% ceria coating [103]. The MCFC unit cell was tested with modified anodes on H$_2$ fuel with up to 100 ppm of H$_2$S. The cell delivered power densities of about 105 mW cm^{-2} after about 175 h of operation as compared to 60 mW cm^{-2} for an unmodified
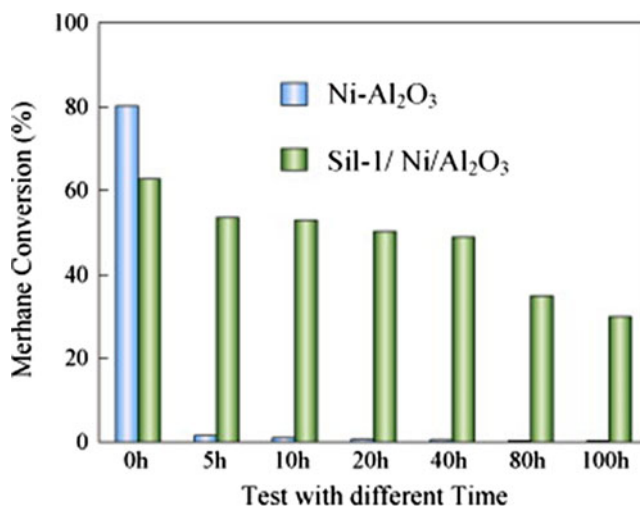

Fig. 12 Methane conversion rate improvement with zeolites in DIR catalysts. Figure reprinted from [101] with permission from the publisher

cathode with 80 ppm of H_2S. The protective behaviour of the Ce coating is attributed to the reaction of Ce with H_2S to form an oxysulphide species Ce_2O_2S, which is sulphur sorbent. Combining the electrochemical performance with stability of ceria-coated anodes as determined by immersion tests in a carbonate melt indicates that these anodes might be promising candidates for sulphur-containing fuels. It should however be noted that although the power densities of the cell in Devianto's work were higher than for the bare NiO anode, the coated anode still demonstrated degradation in power density from 120 to 105 mW cm^{-2} and thus presents scope for further improvement. In recent years bio-ethanol has emerged as a fuel of interest; as in recent decades, it can be obtained from fermentation of sugar cane, rice, crops and biowastes, etc. and it contains from 5 to 20 wt% ethanol. A US patent by Yoon et al. reported a method and performance of a bio-ethanol-fuelled MCFC with coated catalysts [104]. The anodes were coated with transition metal catalysts such as Ni or Cu, Fe supported on oxides such as ZnO, Al_2O_3 and CeO_2, etc. using methods such as spray coating and hot pressing. The thickness of catalyst layer was about 140–160 μm. The power densities up to 90 mW cm^{-2} at about 130 mA cm^{-2} were reported for 20 % bio-ethanol fuel (balance N_2) at 650 °C with 15 wt% Ni/MgO catalysts prepared via co-precipitation and coated on Ni–10 wt% Cr anode using hot pressing. The performance is claimed to be stable during 100 h of testing with a 20 % ethanol fuel. In addition to resistance to alkali and sulphur tolerance, the coking resistance is also important for hydrocarbons considering the tendency of Ni to promote carbon filament formation. One of the approaches taken by the SOFC community to develop carbon/sulphur-resistant anodes is by employing ceramic anodes such as titanates and manganates. These anodes offer superior sulphur tolerance and resistance to coking as compared to Ni-based cermet anodes but they lack the electrocatalytic activity and their conductivity is significantly lower than NiO anodes [105]. Furthermore, it is well known that in the case of SOFCs, the use of precious metals in few weight percent in conjunction with oxides significantly improves the performance as well as coking resistance. For MCFC applications, not many ceramic anodes have been tried, perhaps because of the lack of electrochemical activity at lower temperatures and poor conductivity. Tagawa et al. reported performance of methane-fed MCFC with lanthanide oxides (La_2O_3 and Sm_2O_3) and titanium composite anodes [106]. The lanthanides provide catalytic activity for fuel conversion, and fine Ti powder provided the required electronic conductivity. Based upon obtained open circuit voltage (OCV) and theoretical OCV calculations for methane oxidation, they claimed the direct oxidation of methane over these anodes and suggested that the reaction path is via an electrochemical oxidative coupling of methane on the oxides. However,

the actual cell testing under load needs to be carried out to evaluate the suitability of these anodes in long-term MCFC operations. In a recent review of MCFC electrode materials by Antolini, the Ni/Al_2O_3 catalyst promoted with up to 0.3 wt% Ag is suggested as the best solution at present for coking [107]. The work carried out by Parizotto et al. showed that addition of 0.3 to 0.5 wt% Ag improves the stability of reforming catalysts in tests carried out for 6 h; however, the conversion activity was only 20 % for methane fuel fed under steam/carbon ratio of 0.5. The improved stability is attributed to the change in the surface structure of Ni due to the decrease in the Ni ensemble because of Ag [108].

For DIR catalysis, it appears that the placing of catalysts directly on the anode would be more economical compared to placing the catalysts in fuel channels as the later requires pelletization of catalysts and modification to the cell hardware. While placement of the catalyst on the anode obviously makes it more susceptible to poisoning due to carbonate melt vapours. Recently Li et al. reported the effect of the location of the catalyst in DIR MCFCs [109]. They used $Ni/MgSiO_3$ for reforming methane fuel. Up to 82 % methane conversion was obtained in the cell testing for a fresh catalyst. For cell testing, the catalyst was applied in two ways: (1) placement in fuel channels and (2) direct coating of catalyst on the anode (Ni–10 wt% Cr) by hot pressing. The electrochemical performance data obtained show the cell configuration where catalyst placed in fuel channels offered better stability after 1,200 h of testing on methane fuel (Fig. 13).

Other approaches to mitigate the problem of deactivation of DIR catalysts are: indirect internal reforming (IIR) and the use of a separator plate. In IIR, the reforming catalyst unit is kept in thermal contact with the MCFC unit with exit ports of the IIR unit connected to entry port of the anode [110]. In this arrangement, the catalyst is not exposed to the anodic atmosphere and thus it increases the life of the catalyst. Furthermore, the IIR arrangement also offers a better thermal gradient in the stack as compared to DIR. However, the efficiency of IIR unit is lower than DIR as hot steam formed at the anode is not used in IIR. To combine the advantages of both IIR and DIR systems, the commercial developers FCE Inc and MELCO used a hybrid approach (Fig. 14). The partially reformed fuel from IIR catalyst is reformed further at the anode with DIR. The hybrid design improves the thermal distribution inside the cell and thus improves the overall performance and stability [78].

MCFC matrix

The MCFC matrix acts as a separator between the anode and cathode holding the electrolyte. It is sandwiched between

Fig. 13 Comparison of placement of DIR catalysts **a** on anode and **b** in fuel channels with Ni/MgSiO₃ on voltage degradation at 650 °C, with a steam-to-carbon ratio of 3:1. Figure reprinted from [109] with permission from the publisher
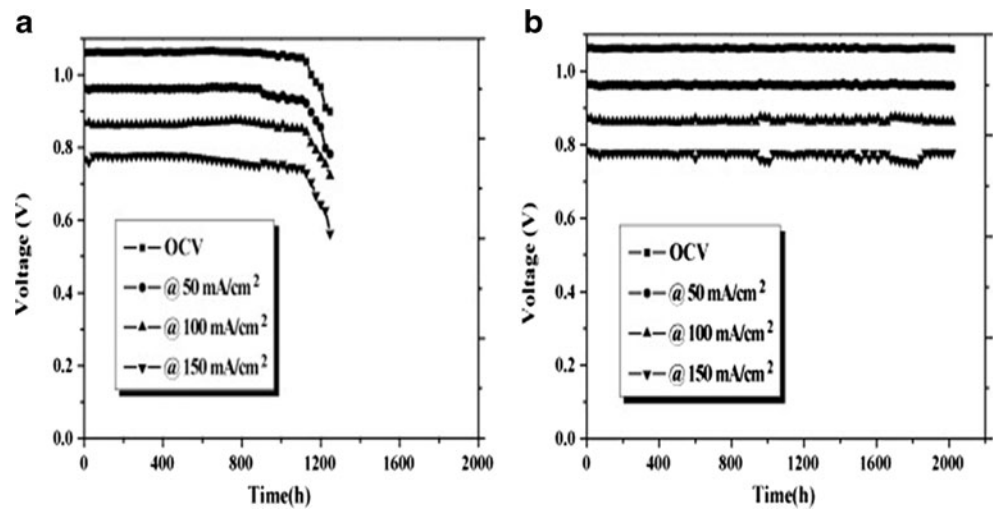
the anode and cathode, and the carbonate melt is immobilised by capillary pressure (typically >0.2 MPa). The pore structure and porosity of the matrix material are required to be carefully controlled. The suitable range of matrix porosity in order to obtain optimum electrical conductivity can be estimated by the Meredith–Tobias equation as:

$$\rho = \rho_0 \delta^{-2} \tag{11}$$

where ρ is the specific resistance of the matrix, ρ_0 the specific resistance of the electrolyte and δ is the matrix porosity [111]. The pore diameter of the matrix is also critical and the suitable pore diameter (radius) required to retain the electrolyte under the pressure gradient (ΔP) between the anode and cathode can be calculated from the Young–Laplace equation as
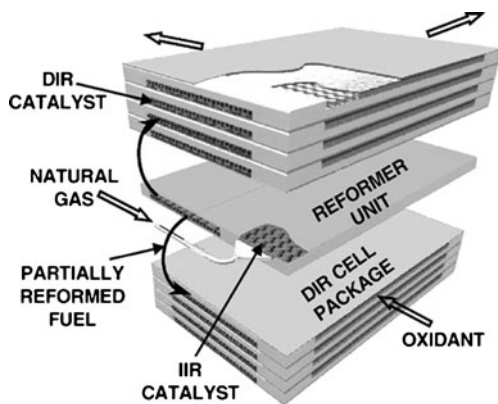
$$\gamma = \frac{2\sigma \cos\theta}{\Delta P} \tag{12}$$

Fig. 14 Hybrid direct internal reforming (*DIR*) and indirect internal reforming (*IIR*) approach developed by FCE to improve the stability of reforming catalysts. Figure reprinted from [90] with permission from the publisher

where σ is the surface tension coefficient of the electrolyte, θ the contact angle between the electrolyte and the matrix, γ the maximum pore radius in the matrix and ΔP is the pressure difference between the anode and cathode compartments [112]. Recently, Zhou et al. have reported optimum porosity and pore diameter calculations for the α-LiAlO₂ matrix based upon Eqs. 11 and 12 and concluded that the matrix should have a pore diameter less than 7.94 μm (0.1 bar pressure differential) and porosity of 40–70 % for longer lifetime [113]. The eutectic mixture of Li/K or Li/Na is state-of-the-art electrolyte materials. The ionic conductivity and electrode wettability (as defined by contact angle) are key criteria for the electrolyte materials. The ionic conductivity of Li/Na system is higher than Li/K system as verified by Morita et al. in bench-scale cell tests shown in Fig. 15 [114]. Not only does the Li/Na electrolyte decrease ohmic losses inside MCFC but also improves the cathode stability as it is more basic as compared to Li/K. Yoshiba et al. demonstrated 10,000 h of operation of a 10-kW class MCFC with Li/Na electrolyte and stamped matrix with voltage degradation as low as 0.3 % per 1,000 h [115]. Although the Li/Na electrolytes are expected to perform adequately for 40,000 h operation, there is still room for further improvement in the electrolytes considering lower wettability of Li/Na as compared to Li/K electrolytes resulting in higher cathodic polarisation [19].

For the matrix, traditionally the γ-lithium aluminate (γ-LiAlO₂) is the material of choice. The major materials issues with LiAlO₂ matrix are: particle growth, pore coarsening and allotropic transformation from the γ-phase to α-phase accompanied by a change in the density during the MCFC operation. As the α-phase is denser (3.4 gcm⁻³) than the γ-phase (2.6 gcm⁻³), the allotropic transformation increases the pore volume thus resulting in the electrolyte depletion in the matrix [78]. The loss of electrolyte volume reduces the ionic transport and causes fuel crossover
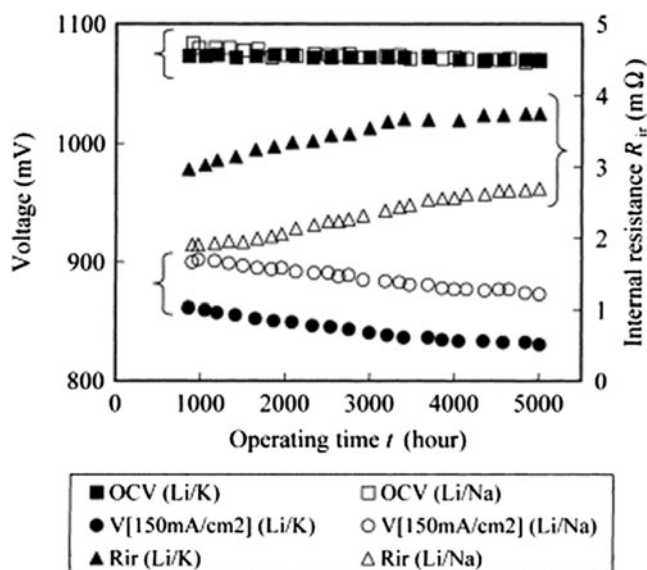
Fig. 15 Performance comparison in terms of voltage degradation and cell internal resistance of MCFC with Li/K and Li/Na as electrolytes, at different current densities. Figure reprinted from [114] with permission from the publisher

resulting in voltage degradation. The phase transformation is believed to be initiated with dissolution of smaller particles of matrix in the carbonate melt [116]. The dissolved material then deposits on larger particles resulting in further growth (dissolution–deposition growth). The investigations by Takizawa et al. supported the dissolution–deposition route as a mechanism of particle growth and/or phase transformation in the MCFC matrix [117]. Clearly, the rates of particle growth and phase transformation are strongly dependant on the rates of solubility, diffusion and precipitation of the lithium aluminates in the carbonate melt. The studies at Toshiba Inc (Japan) indicated that the γ-LiAlO$_2$ phase is stable in air at the MCFC operating temperature but it loses its stability in MCFC atmosphere and allotropic transformation to α-phase takes place [118]. They reported the α-phase is stable even at 700 °C and operated over 7,550 h under 0.1 atm. CO$_2$ partial pressure. SEM observations revealed only a slight increase in pore diameter after testing, indicating that electrolyte retention is sufficient. Similar findings were reported by Terada et al. on stability as well as solubility of LiAlO$_2$ in carbonate melt [119]. Their studies indicated that the particle growth of lithium aluminates occur faster at higher temperatures as expected, in low CO$_2$ partial pressure and in a strong basic melt. Hence for long-term stability, a higher partial pressure of CO$_2$ and a low basicity carbonate melt are desired. However, these conditions are unfavourable for cathode (NiO) charge transfer and stability; hence, the proper balance of CO$_2$ partial pressure is required for practical operation. The addition of additives to the carbonate melt can be effective in suppressing the matrix particle growth. Terada et al. reported the

effect of oxide additives such as K$_2$WO$_4$, MgO, Ga$_2$O$_3$, etc. on the matrix stability and found that the addition of K$_2$WO$_4$ can inhibit particle growth and the phase transformation of matrix significantly [120]. The performance of unit cells with α-LiAlO$_2$ has been investigated by the researchers and found to be acceptable for use in MCFC [121, 122]. Based upon outcomes of 20,000 h of stability studies by Oza et al., α-LiAlO$_2$ appears to be suitable for 40,000 h target lifetime [78]. As a result of the studies on phase transformation and evaluation, the use of α-LiAlO$_2$ to replace γ-alumina as the MCFC matrix is gaining increasing attention from the MCFC community. However, the commercial manufacturers such as FCE, MELCO, etc. continue to use γ-alumina possibly because of their expertise and prior experience with γ-alumina.

The conventional fabrication method of the MCFC matrix is tape casting. It is well known that the properties of the final product from the tape casting process are affected greatly by the characteristics of the starting ceramics used, binders, dispersant, etc. The tight control over the fabrication processes is especially important for commercial cells with a large area matrix. It is a common experience of ceramicists that the higher solid content in the starting slurry leads to cracking in the large area components. Also the fragility of the tape cast matrix is the issue in commercial handling. Recently Ferrari et al. reported that the plastic extrusion technology may be more suitable for fabrication of the MCFC matrix with tighter control and less surface defects as compared to tape casting [123].

In addition to particle growth and fabrication issues, other issue with the matrix materials is the mechanical strength to cope with stacking load and thermal cycling. In MCFC, the matrix undergoes mechanical stress due to the mismatch between the coefficients of thermal expansion between the LiAlO$_2$ and electrodes. Since the mechanical strength of pure LiAlO$_2$ is found to be inadequate for long-term practical use, various approaches have been taken to improve the strength and crack resistance. Some of these approaches are the matrix reinforcement with ceramic fibre or rod-shaped particles and the use of a second phase such as large γ-LiAlO$_2$ particles as crack arrestors [124, 125]. Lee et al. have reported the addition of aluminium salt (aluminium acetylacetonate) during the slurry preparation for the matrix tape to improve its mechanical strength while retaining acceptable porosity [126]. At the temperatures above 420 °C, the salt decomposes to form Al$_2$O$_3$ which in turn reacts with matrix to form LiAlO$_2$. The resulting phase forms a neck between the matrix particles, improves the connectivity and as a result an abrupt increase in mechanical strength is observed. The increase in the strength is also observed with metallic Al particles as observed by Kim et al. [127]. They tested the mechanical strength and stability of tape cast MCFC LiAlO$_2$ matrix with added 30 wt% metallic

aluminium with 3 and 30 μm particle sizes. While both matrices showed comparable pore size and pore volume, the bending strength (0.2 kg mm^{-2}) of the matrix with 3 μm additives was found to be twice than that of 30 μm particles. The metallic aluminium gets converted into alumina at 650 °C in the presence of cathodic oxygen and Li$_2$CO$_3$ melt. Since the oxidation process consumes the electrolyte carbonate melt, it was recommended to add Li$_2$CO$_3$ in the matrix slurry during the tape casting so that no additional electrolyte in the matrix is consumed during in situ oxidation. Recently, Choi et al. reported the comparison of stability of alumina reinforced γ and α matrices at 650 °C in MCFC atmospheres for 20,000 h [128]. It was concluded that alumina-added α-LiAlO$_2$ is the most stable phase among all allotropes.

It can be inferred from the recent studies that α-LiAlO$_2$ with additives such as alumina would be an effective MCFC matrix with adequate stability and improved mechanical strength due to alumina reinforcement.

As the alumina matrix offers adequate performance and is cost effective, not many alternative materials have been explored for the MCFC matrix. Recently Patil et al. investigated the stability of Li$_2$ZrO$_3$ and ceria in Li/K electrolytes for 5,000 h. Their findings indicate the Li$_2$ZrO$_3$ as well as cerium oxides could be potential candidates for MCFC applications [129]. The matrix material such as ceria is interesting considering the fact that the composite systems of ceria molten carbonate electrolytes have been reported to show multi-ionic conductivity (CO$_3$ and O^{2-}) [130]. If such a phenomenon can be utilised in the MCFC matrix with ceria- or zirconia-based materials, the power density of MCFC can be improved. However, the lower mechanical strength of ceria and stability under reducing atmosphere would be a concern especially at temperatures above 700 °C.

Bipolar current collectors and metallic components

Apart from porous components discussed so far, bipolar plates and current collectors are critical metallic components for commercial MCFC stacks. In fact for commercial MCFC systems, up to 55 % of the material content could be the metallic hardware (for the complete system) which includes cell, stack and balance-of-plant materials [131]. The stability in corrosive carbonate atmosphere at high temperature, good electrical conductivity and low contact resistance with the electrodes are desired characteristics of bipolar plates and current collectors. The bipolar plates are exposed to different atmospheres on the anodic side, cathodic side and wet seal area of MCFC, and hence the ideal material for bipolar plate current collectors should have acceptable corrosion resistance for all of these atmospheres. Although Ni suitably meets these requirements, the high

cost of pure Ni and the lack of desired mechanical properties hinder its use in commercial systems. The stainless steels like 310 S (24–26 wt% Cr) and 316 L (16–18 wt% Cr) have emerged as materials of choice for MCFC hardware [132]. However, the hot corrosion in the presence of the carbonate melt is the critical issue with these materials for long-term operation. During the period of initial operation, the mechanism of corrosion in these steels is normal corrosion involving scaling via the formation of a layer of iron oxides on the chromium-rich oxide layer. After medium time exposure, the lithiation of the iron oxide or Cr oxides takes place followed by the formation of stable phases between Na, K and iron or chromium scale [132]. Furthermore the acidic or basic dissolution of scale takes place depending upon the environment exposed to the un-corroded metal. The scaling layer is porous and exposes the active sites for corrosion by penetration of molten salts. Furthermore, the phenomenon like sensitization causing Cr depletion near the grain boundaries can occur in MCFC environments [78]. The fundamental electrochemistry of the corrosion phenomenon in MCFC systems is complex and not completely understood as yet. The disagreement between the data such as exchange current density and polarisation resistance by various corrosion characterization techniques such as linear polarisation techniques, Tafel analysis and EIS further adds to the complexity [133]. In late 1990s, Spigel et al. reported a study on hot corrosion of various steels including high alloy steels in cathodic environments and reported that the corrosion of these materials proceed via the formation of superoxide (O$_2^{2-}$) ions [134]. If the corrosion proceeds via the formation of superoxide ions, the concentration of corrosive species would be uniform in the carbonate melt and fluxing would not be required. Frangini reported the analysis of the corrosion process based upon potentiodynamic polarisation measurements and EIS studies [135]. It was found that under high anodic currents, acidic dissolution of the passive protective layer occurs, while for high cathodic currents, basicity increases with oxide ion build-up in the carbonate melt.

In a typical MCFC, the anodic atmosphere is more corrosive than the cathodic atmosphere due to continuous reduction of oxide scales by hydrogen. Also, the cathodic corrosion is less under loading than under open circuit conditions, while the situation is reversed for the anode side corrosion, i.e. the anodic corrosion is more severe under load than open circuit conditions [136]. Furthermore, it was also observed that on the anode side, corrosion rates are higher at the fuel outlet area than at the fuel inlet because of higher temperature of exit gases and presence of alkali vapours at the exit [137]. It is also possible that the hydrogen gas from the anode side diffuses to the cathode side via the steel plate as typical thickness of the plate is around 0.3 mm [138].

These characteristics of MCFC make the material's choice for a suitable bipolar plate complicated. Apart from the loss of material itself, the hot corrosion of these components also causes loss of electrolyte in the matrix because of the reaction with the carbonate melt and may also cause short circuiting of the cell if corrosion products formed are electrically conductive. The loss of electrolyte from metallic corrosion after 6,000 h of operation was estimated to be 6 % of total electrolyte loss during MCFC operation [139]. To protect the steel, the electrolytic coating or cladding of steel with Ni emerged as the promising compromise between price and stability. This material is believed to have sufficient corrosion resistance for target lifetimes (40,000 h) if the coating thickness is high enough, but the cost of such anodes is high and more cost-effective materials are sought. Furthermore, there is a possibility of mechanical failure of the coated component because of the hardness increase induced by carburization in the base metal grains or in the grain boundaries below the Ni coating as indicated by Durante et al. [140].

The approaches to mitigate the problem of corrosion include use of additives in molten carbonates, using alternative corrosion inhibitor coatings and alloying of the steels. The oxide additives to molten carbonate melt such as alkali earth oxides or lanthanides increase the oxygen solubility of the carbonate melt as mentioned in "MCFC cathode" section. The increased basicity drives the open circuit potential for corrosion to positive side, thus indicating improved corrosion resistance. Also these additives may alter the passivation properties by competing with Li to reach the active corrosion site and by increasing the melt basicity [141]. Frangini et al. reported the effect of alkaline earth additives such as Ca, Ba and Mg added over a wide range of concentrations on the corrosion of 316 L stainless steel (SS) electrode immersed in Li/Na carbonate. It was concluded that in lower amounts (1.5 wt%) the mechanism of corrosion remains the same as that of the melt without additives. When the amount of additives is increased to 5 to 10 wt%, the 316 L SS becomes more corrosion-resistant with the corrosion mechanism changing from a cathodic to anodic type of corrosion. While the additives may improve the corrosion resistance, the high amounts of additives in the electrolyte are detrimental to the overall MCFC performance. The approach of coating SS with conductive ceramics such as $LiFeO_2$ or LSC using simple sol–gel type methods appears to be a promising alternative to improve the corrosion resistance. However, in the studies conducted by Frangini et al., the microstructure of the coated steels revealed that these coatings can only provide temporary corrosion protection [132].

For the current collector application along with the high corrosion resistance, minimum contact resistance between the electrodes and metal is desired especially on the cathode side where the oxide scale formation increases the contact resistance between metal and cathode. Colón-Mercado et al. reported the cobalt-coated titanium alloy Beta 3 (Ti77.5/ Mo12/Zr 4.5/Sn 4.5) as the cathode current collector [142]. The electrodes were heat treated at 400 °C to promote the formation of an oxide layer and was electroplated with Co before testing. They found that Co layers offer a transient protection and eventually dissolve in the carbonate melt exposing the underlying oxide layers. The corrosion resistance as determined by EIS was improved by an order of magnitude (133 Ω) from the corrosion resistance of 316 L SS (4.3 Ω). Considering the well-established manufacturing processes for titanium alloys, these materials can be an attractive candidate as a current collector in MCFC; however, the cost of electroplating (Co plating) could be an issue.

Over 70 different Ni-based-, Co-based- or iron-based alloys have been investigated for the steel hardware of MCFC by various manufactures and developers [78]. The materials used in commercial products are mostly proprietary alloys. The Ni-based superalloys can be used for these applications but the cost of these alloys is high. Studies to improve the corrosion resistance of stainless steels and nickel-based alloys in MCFC atmospheres confirmed that the addition of aluminium improves corrosion resistance and this method is cost effective as well [143]. The addition of Al leads to the formation of oxide layer on the cathodic side and this hinders the use of alloys containing Al as bipolar plates. The four-probe conductivity measurement experiments conducted by Biedenkopf et al. demonstrated that even very small amount of Al leads to increase in ohmic resistance by order of magnitude [144]. Parezanović et al. conducted extensive studies on Co-, Mn-, Mo-, Si- and Ni-added stainless steel as cathode current collectors [145]. They found that alloying elements such as Co, Ni and Mn forms a p-type conductive oxide layer which is beneficial for conductivity while ferritic stabilisers such as Si and Cr improve corrosion resistance. The best corrosion resistance was obtained for alloy 'V152' with 12.2 % Mn, 17.6 % Cr, 3.03 % Mo, 2.95 % Ni and 0.5 % Si with electrical resistivity of 0.12 $\Omega\ cm^2$ in MCFC environment. Fine tuning of the compositions in these type of alloys (conductive spinels forming alloys) would be possibly the best approach for developing MCFC cathode current collectors. For the anode side current collectors, Ni-claded stainless steel appears to be an optimum choice. Randström et al. of KTH (Sweden) compared the commercial high-temperature alloy steel, yttria-doped Ni and stainless steel claded with Ni as the anode side current collector. They concluded that the trade-off between performance (contact resistance) and cost leaves the bimetallic materials based upon Ni-claded austenitic stainless steel as the optimum choice for MCFC hardware [146]. The review of literature clearly suggests that at present, substantial R&D opportunity exists for the development

of stable and cost-effective alloys or cermets for MCFC hardware applications.

Conclusion

The MCFC technology is maturing at fast pace for commercialization. There are few companies over the world who have demonstrated the operation of the MCFC systems from kilowatt to megawatt range, either at a pilot scale or at a fully commercialisation stage. Lifetime operation of pilot plants has been demonstrated for up to 30,000 h with electric efficiencies of up to 50 %. However, significant development work is required to be performed to improve the power density of MCFCs and tackle the materials issues such as cathode dissolution, corrosion of cell hardware such as bipolar plates and current collectors, and electrolyte loss due to creep in the matrix and electrodes. Among various approaches which are being explored by researchers, the application of spinel-coated cathodes such as doped cobalt oxide or rare earth-doped strontium oxide could be a promising solution to avoid cathode degradation if technology scale-up can be achieved. The use of coated nickel particles with core–shell structure for tape casted cathodes could be an immediate solution for achieving improved lifetime. The demonstration of MCFCs with coated cathodes for more than 10,000 h and post-mortem analysis would be necessary to prove the stability of these cathodes and confirm the retention of adequate porosity. In case of anode, while Ni-based materials satisfy most of the requirements, the stability and creep resistance can be further improved with the addition of intermetallic phases. The additives may also enhance the wetting on anodes by electrolyte; however, the effect of added phases on long-term electrochemical performance should be investigated for these materials to qualify as an anode in practical MCFCs. For operating MCFC on real world hydrocarbon-based fuels, further development is required on internal reforming catalysts or system design to avoid the issue of deactivation of catalysts and sulphur poisoning. The long-term stability evaluation of novel zeolite-type catalysts or ceria-doped anodes could confirm the applicability of these anodes as MCFC DIR catalysts. For the MCFC, matrix α-alumina appears to be a suitable material; however, commercial manufacturers continue to use either α-alumina or β-alumina depending upon their experience in fabrication and pot tests. For MCFC, hardware Ni-claded austenitic steels and alloy steels like V152 are preferred choices; however, further improvements are sought for a cost-effective solution to the corrosion problems. In conclusion, significant opportunities exist for materials R&D to achieve the lifetime goal of 40,000 h and meet the target cost of $2000 per kW in conjunction with developments in systems aspects for a MCFC plant.

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