Short communication

MCFC versus other fuel cells—Characteristics, technologies and prospects

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Abstract

Characteristics of molten carbonate fuel cell (MCFC) were critically compared to these of polymer electrolyte membrane fuel cell (PEMFC), alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC) and solid oxide fuel cell (SOFC). In comparison to the other fuel cells, the MCFC operates with the lowest current densities due to limited zones of effective electrode reactions and low solubilities of oxygen and hydrogen in molten carbonates; also it has a thickest electrodes–electrolyte assembly. In consequence, the applications of MCFC are almost limited to stationary power generators. Although the MCFC stationary power generators have now approached high technological level of precommercialization, in the future they may face a serious contest from SOFC and PEMFC, for which improvement of operational parameters is believed to be achieved easier.
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1. Fundamentals of molten carbonate fuel cell

Amongst all the hydrogen–oxygen fuel cells, the MCFC is the only one, which employs a molten salt electrolyte. To keep the electrolyte in liquid state, the cell must operates above $500\,^\circ C$ (the standard operation temperature is $650\,^\circ C$) [1]. Therefore, a power unit with the MCFC stack has to be equipped with a precise temperature controller, which provides the stable conditions of the cell operation and, in extreme cases, prevents the electrolyte from either freezing or intensive vaporization.

The electrochemical reactions occurring in the MCFC are

$$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^- \tag{1}$$

at the anode, and

$$(1/2)O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-} \tag{2}$$
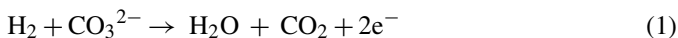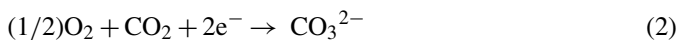
at the cathode. On the contrary to the other fuel cells, the MCFC requires supply of CO_2 to the cathode. Therefore, a MCFC generator is generally equipped with a "CO_2 transfer device". It is usual practice that a part of anode exit gases, after complete combustion, is introduced into the cathode inlet gas stream.

Water vapour, the product of hydrogen oxidation, is formed in the MCFC at the anode of the cell, hence the outlet anodic gases content more water than the inlet gases. The higher partial pressure of water leads to an additional decrease of the cell voltage and cell efficiency. This loss of efficiency is a part of Nernst losses resulted from changes of gas composition due to the electrochemical processes.

2. Characteristics of MCFC in comparison to the other fuel cells

The polarization curves for various hydrogen–oxygen fuel cells are presented in Fig. 1. They are averaged over performances of single cells in the most frequent conditions of operation for a given fuel cell type [2–4]. A striking feature of the voltage versus the current density dependence for the MCFC is its linear character. The linear character of polarization dependence is usually attributed to the ohmic drop in the cell, however, in the case of MCFC, the reason for this behaviour remains still unclear [5,6].

For the MCFC, the polarization curve is the steepest among all the hydrogen–oxygen fuel cells. Therefore, within the group of the fuel cells considered, the MCFC has

• the lowest current densities at high power range,

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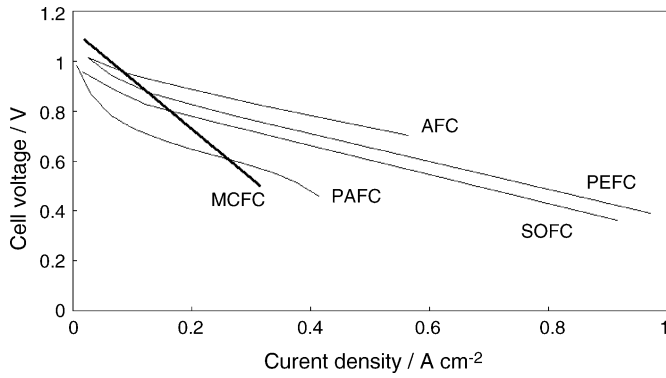 *E-mail address:* ptomczyk@uci.agh.edu.pl.

Fig. 1. Polarization curves for various hydrogen–oxygen fuel cells.

- high efficiency of the cell in the limited range of low current densities, up to ca. $150\,mA\,cm^{-2}$.

The thicknesses of electrodes and electrolytes are compared for various fuel cells in Fig. 2 [4,7–10]. In this figure, apart from the MCFC, PAFC and PEMFC, three types of solid oxide fuel cell in two different configurations are presented: TSOFC is the tubular cell, which operates at ca. $1000\,°C$ and ITSOFC (electrode or anode supported) is the intermediate temperature SOFC with flat-plate design, whose operational temperature is $600–800\,°C$. As can be seen, the molten carbonate fuel cell has one of the thickest electrodes–electrolyte assembly (1–3 mm) and definitely the thickest electrolyte (0.5–1.5 mm) among all the hydrogen–oxygen fuel cells. Thick electrolyte neutralizes the phenomenon of NiO cathode dissolution in molten carbonates, which may lead to formation of Ni dendrites and consequently to short circuit between the electrodes [11,12]. Fortunately, due to the high conductance of molten salts, the ohmic drop in the MCFC remains still acceptable even if a matrix electrolyte is relatively thick.

All the mentioned above characteristics of MCFC: (i) sophisticated auxiliary system (precise temperature control, CO_2 transfer device); (ii) low current densities and (iii) thick electrodes–electrolyte assembly cause that this type of fuel cell is almost exclusively designed for stationary power generators. Some niche applications for high power MCFC units are also possible, for example ship service power plant [13]. Accord-

ing to the technological level already achieved, the state-of-the art MCFC can soon appear at the marketplace as a commercial product. Since the PAFC PC 25 unit (ONSI) is considered to be valuable but bygone experience [14,15], the main competitor in sector of stationary power generators is now SOFC. It is also very likely that a new PEMFC unit will soon appear, following pathway of 250 kW demonstration plant of Ballard Generation System [16,17].

On the other hand, the MCFC generators, whose output power is to be over several megawatts, may face sever competition from traditional power plants that use heat engines. The efficiencies of power plants with advanced turbine system and gas turbine combined cycle are similar to these of fuel cells but their positions at the market place have been established for long time and their lifetimes are much longer than the lifetimes of nowadays fuel cells [4,18]. Therefore, the most attractive application of MCFCs is medium scale stationary unit (from 100 kW to 10 MW) for distributed power and heat generation. For this application, the MCFC must meet at least two particular requirements: improve their operational parameters by decrease of the cell polarization under load, also their material and production costs must be reduced.

3. Performance of porous electrodes in fuel cells

The voltage losses for various fuel cells (MCFC, PAFC, PEMFC, DMFC—direct methanol fuel cell and ITSOFC) are depicted in Fig. 3 [4,7,19–21]. In the case of MCFC, performance improvement is possible mainly by reducing cathode polarization. Anode polarization has marginal effect on output voltage of the cell, reduction of Nernst loss is difficult because results from a fuel and oxidant consumption and ohmic drop is mainly due to the thick electrolyte. As can be seen from Fig. 3, the performance of other types of fuels cells also suffers from sluggish kinetics of oxygen reduction. The main parameters affecting the oxygen reaction in MCFC, PAFC, PEMFC and ITSOFC are collected in Table 1.

In the case of MCFC, the cathode overpotential that occurs during operation of the cell is distinctly lower than in the cases of PAFC and PEMFC. However, considering quantities collected in Table 1 [1,20–23], one may expect that the relative differences between the magnitudes of cathodic overpotentials for
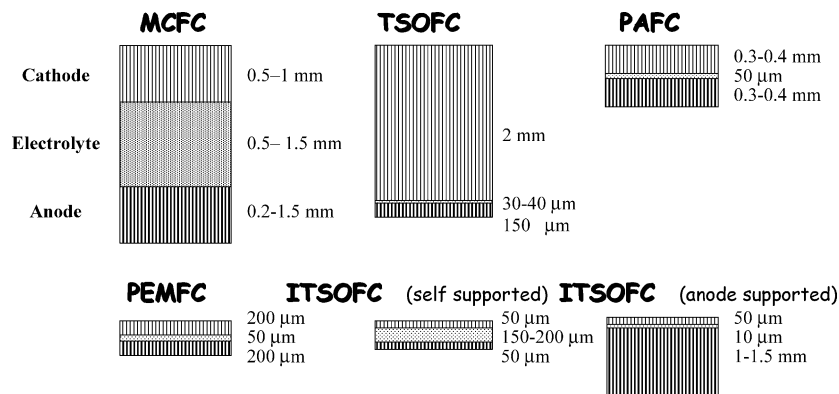

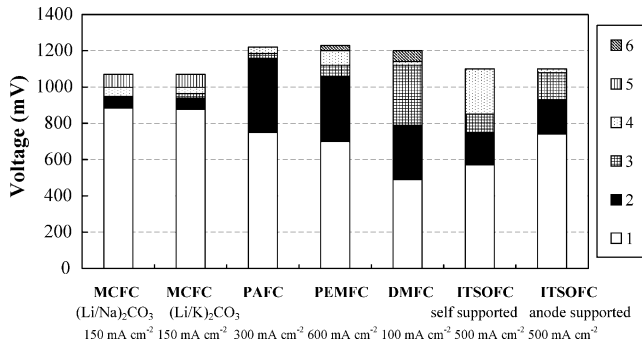Fig. 2. Thickness of electrodes and electrolytes for various hydrogen–oxygen fuel cells.

Fig. 3. Voltage loss contributions for various fuel cells: (1) cell voltage, (2) cathodic polarization, (3) anodic polarization, (4) ohmic polarization, (5) Nernst loss and (6) effect of fuel crossover.

Fig. 4. Distribution of molten carbonate electrolyte in porous electrodes of MCFC as a result of balance in capillary pressure.

these fuel cells should be even larger. Effectiveness of the cathode operation in the PAFC, PEMFC and SOFC is improved by using special techniques of electrode fabrication, which are useless in corrosive environment of molten carbonates. These techniques are aimed at either extending three phase region, where the highest current is produced in electrochemical reaction or enlargement of reaction zone.

A stable electrolyte/gas interface in the MCFC porous electrodes is established exclusively due to balance in capillary pressures. The diameters of the largest flooded pores in these electrodes are related by the equation [4]:

$$\frac{\gamma_a \cos\theta_a}{D_a} = \frac{\gamma_c \cos\theta_c}{D_c} = \frac{\gamma_e \cos\theta_e}{D_e} \qquad (3)$$

where γ is the interfacial surface tension, θ the contact angle of the electrolyte, D the pore diameter and subscripts a, c, and e refer to the anode, cathode and electrolyte matrix, respectively. The distribution of molten carbonates in the electrodes and electrolyte matrix is illustrated schematically in Fig. 4.

On the contrary to the MCFC, more sophisticated and ingenious constructions of the porous electrodes have been applied in the PAFC, PEMFC and SOFC to enhance their performance. Namely

- *PAFC*. Electrodes are made of carbon materials, which serves as a structural support for an electrocatalyst layer and current collector. The composite structure consisting of a carbon black (hydrophilic)/PTFE layer (hydrophobic) on carbon
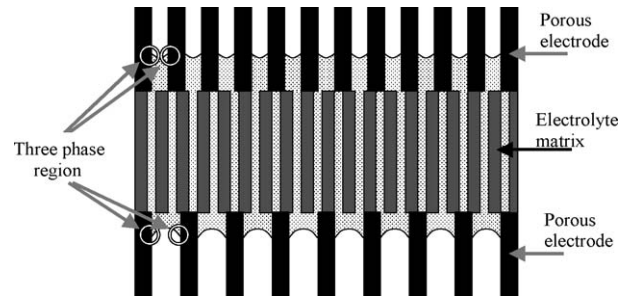
paper substrate forms a stable, three phase interface of liquid electrolyte, electrode and gas phase [24]. Schematic diagram of a single pore in the PAFC is shown in Fig. 5a.
- *PEMFC*. Also in this fuel cell, carbon materials are main components of electrode structure. To extend reaction zone, particles of catalyst are usually impregnated with a thin layer of polymer electrolyte and hot pressed to the membrane [24] (Fig. 5b).
- *SOFC*. To enhance performance of this fuel cell, mixed ionic-electronic conductors (MIEC) are employed as electrode materials [25]. In the MIEC electrodes, oxygen ions can be transported through the bulk of the electrode to the electrolyte interface; this way the reaction zone can be extended to the whole surface of the electrode (Fig. 5c).

4. Prospects of MCFC

As far, the discussion performed in this paper has unintentionally revealed the weak points of MCFC. However, the MCFC has also some advantages over its main competitors—the PEMFC and SOFC: (1) the MCFC operating temperature is 650 °C, optimal for internal reforming and exploiting of useable heat. The operating temperatures of PEMFC is too low for internal reforming and TSOFC is too high to use cheap, steel elements: (2) there is no need for using noble catalyst in the MCFC on the contrary to the PEMFC; (3) CO is a useable fuel for the MCFC, whereas in the PEMFC is a poison for Pt catalyst; (4) the MCFC has higher electric efficiency than the PEMFC: 45–50% versus 36–38%, respectively; (5) technology of MCFC is more advanced than SOFC, in particular ITSOFC (6) due to liquid electrolyte of

Table 1
Parameters affecting kinetics of the oxygen reduction in MCFC, PAFC, PEFC and ITSOFC

	MCFC	PAFC	PEMFC	ITSOFC[a]
Solubility of oxygen (mol dm^{-3})	1.0, 0.3 × 10^{-3}[b]	3.6 × 10^{-4}	(1–9) × 10^{-3}[c]	–
Diffusion coefficient of oxygen species (cm^2 s^{-1})	1, 2 × 10^{-5}[b]	9.1 × 10^{-4}	(1–8) × 10^{-6}[c]	–
Exchange current (mA cm^{-2})	10–40[c]	0.05	0.000002, 0.0008[d]	200
Electrolyte conductivity (Ω^{-1} cm^{-1})	1, 2[b]	0.15	0.01–0.1[e]	0.1

[a] Operational temperature: 800 °C.
[b] For Li/K and Li/Na carbonate eutectic, respectively.
[c] Scatter of the experimental data.
[d] For two different ranges of overpotential with stable Pt oxides and Pt, respectively.
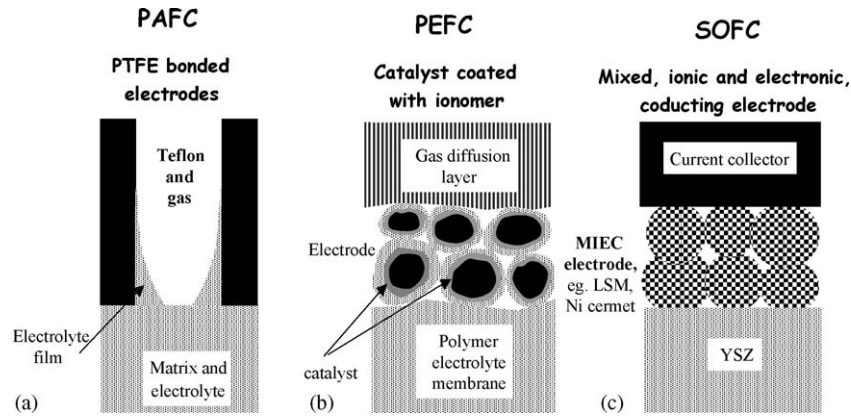[e] Dependent on water content in the membrane.

Fig. 5. Construction of electrodes in: (a) PAFC, (b) PEMFC and (c) SOFC aimed at enhancement of electrode performance.
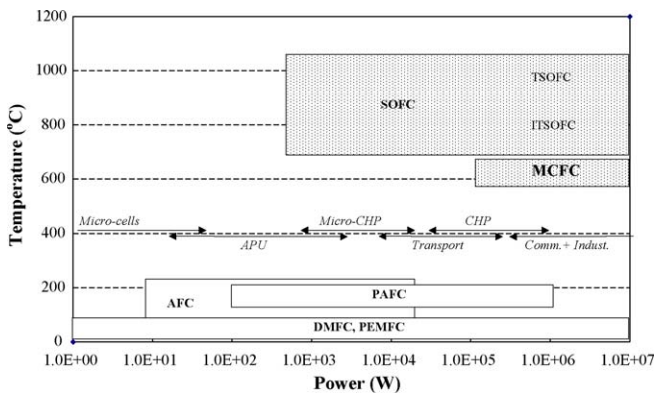

Fig. 6. Position of MCFC at fuel cell marketplace. Shadowed area: possible internal reforming.

MCFC, low contact resistance and gas seal are easy to achieve in contrast to the SOFC and (7) the MCFCs could be successfully applied to CO_2 separation from conventional power plant exhaust gases that is especially beneficial in the possibility of exploiting coal as main fossil fuel (also SOFC technology allows to be applied for carbon dioxide separation in modern power plants) [26].

The intrinsic features of cogeneration of electricity and heat from internally reformed carbonaceous fuels in molten carbonate fuel cell as well as recent progress of this technology, favours the position of MCFC at the marketplace of stationary power and heat cogeneration units (Fig. 6). On the other hand, material and design innovations, which have crucial impact on further development of fuel cells, are potentially much easier to be achieved for the PEMFC and SOFC than the MCFC. Therefore, one may expect severe competition between these technologies in the sector of medium-size power generators in the first decades of 21st century.

Acknowledgement

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