Short communcation

Molten-salt fuel cells—Technical and economic challenges

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Abstract

This paper presents a personal view of the status and research needs of the MCFC and other molten-salt fuel cells. After an overview of current MCFC performance, compared with performance and cost of other fuel cells, improvements in power density and lifetime as well as cost reduction are identified as key priorities to accelerate the commercialization of the MCFC. In spite of its unfavorable public image (compared to, in particular, PEMFC and planar SOFC) MCFC technology has progressed steadily and cost reduction has been significant. Large-scale commercialization, especially in the distributed generation and cogeneration market, remains a possibility but its chances are highly dependent on a forceful and consistent energy policy, for example taking into account the externalities associated with various modes of electric power production from fossil fuels. In spite of steady improvements in performance, important defects in fundamental knowledge remain about wetting properties, oxygen reduction kinetics, corrosion paths and control mechanisms. These must be addressed to stimulate further simplification of design and find solutions to lifetime issues. Recently, alternative concepts of molten-salt fuel cells have been capturing attention. The direct carbon fuel cell (DCFC), reviving an old concept, has caught the attention of energy system analysts and some important advances have been made in this technology. Direct CO and CH_4 oxidation have also been a focus of study. Finally, the potential of nanotechnology for high-temperature fuel cells should not be a priori excluded.

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1. Introduction: the MCFC in perspective among other fuel cells

In spite of public perception, the MCFC has continued to make remarkable advances in both technical and economic respects during the last 10 years. This is in part an effect of the major push given to MCFC technology by worldwide interest and funding in the 1980s and early 1990s. The advance in technical performance consists of many incremental improvements in electrode technology and materials. But they have been made possible by vigorous efforts to carve a clearly defined profile for the MCFC in the distributed generation market, leading to more than thirty demonstration projects on a scale of 300 kW to several MW.

This combined technical and marketing effort is under way in spite of a downturn in the public image of the MCFC and its commercial potential. A major factor in this gloomy perception among potential users was the conjunction, in the mid-90 s, of rather unrealistic assessments of various types of fuel cell

in different stages of development. For example, too optimistic assessments of PEMFC and SOFC were abundant, while assessments of PAFC and MCFC appear in hindsight too pessimistic.

In the last 5 years the economics of fuel cells *in general* are being assessed more soberly. This is largely the result of difficulties in the implementation, limited lifetime and high cost of the PEMFC, which for a long time was the prime contender for early and wise-spread commercialization, especially in transportation. To name just one difficulty, hydrogen, due to its storage and cost barriers, has proved to be an interesting goal – and a boon to the world of research – but not the simple universal fuel of popular science.

In stationary power generation, too, it is safe to say that fuel cells, which in this case means mostly MCFC or SOFC, are still in an expensive early-commercial stage and not competitive with advanced combined-cycle technology. However, the advantages of high-temperature fuel cells are recognized — they are versatile in fuel acceptance, operate with clean exhaust, and achieve high efficiency by system integration (FC-turbine hybrids). Moreover, they have heat/power flexibility.

The general lowering of expectations about commercialization of fuel cells has "flattened the field", to the advantage of the MCFC. Also in a technical sense the field has "flattened".

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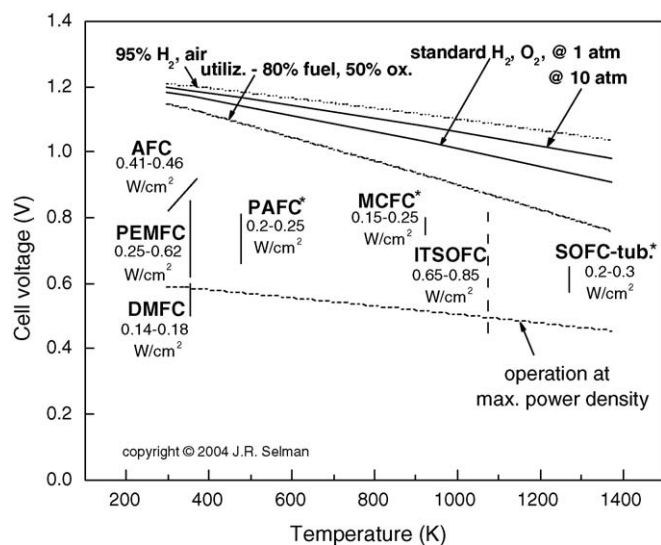 *E-mail address:* selman@iit.edu.

Fig. 1. Typical performance ranges of different types of fuel cells.

The electrical performance of the various types of fuel cell has reached what appears to be a kind of steady state, although further improvements are not excluded. Remarkably, the differences in performance, although they do exist, are less conspicuous than the similarities. This is summarily illustrated in Fig. 1, which shows ranges of electrical efficiency (actual voltage/theoretical voltage) and power densities for the various types of fuel cell as a function of operating temperature.

What Fig. 1 does not show, is the relative state of development and the availability, at present, of the various types of fuel cells. The largest demonstrated units of all types, except the MCFC at present do not exceed 250 kW. This is the case for the PAFC and the tubular SOFC, which have a 35 years history of development. The PEMFC, which emerged more recently (late 1980s), has likewise been demonstrated at a maximum unit level of 200–250 kW, for powering city buses. The planar SOFC, emerging also in the late 80 s, is now approaching demonstration at the 5-kW level in the DOE SECA program. On the other hand the MCFC, at 300–2 MW level, has during the last 10 years been demonstrated, or is still operating, at more than 30 sites in the US, Europe and Japan. It is available pre-commercially in 250–500 kW modules from three major companies, and its application in the distributed generation market appears to be taking hold. Its most successful application thus far is in (1) the high-end residential cogeneration market (hospitals, hotels, shopping centers) and (2) the exploitation of low-cost fuel resources (waste water and landfill gas) as well as industrial cogeneration. The future of the MCFC in cogeneration from biomass fuel, perhaps on a large scale, appears promising.

Of course, the current cost of the various fuel cell types is also not reflected in Fig. 1. As mentioned above, efficiency, although desirable, only indirectly impacts on the cost. But the "leveling" of fuel cell performance suggested by the graph also extends to the cost picture. The mature-production cost of a 200-kW PAFC unit was estimated in 1995 at approximately $ 2500 kW^{-1}, at a production level of 150 MW y^{-1}. This was based on a learning curve with exponent approximately −0.3. But the increase in

production volume and consequent cost decrease did not materialize. Currently commercial PAFC units (UTC's "Purecell") costs in excess of $ 4000 kW^{-1}. For the 50–200 kW PEMFC the current cost is likely to be very similar ($ 3000–4000 kW^{-1} with hydrogen fuel). Optimistic projections dating from 5 to 10 years ago expected a $ 177 kW^{-1} cell and $ 294 kW^{-1} system cost at production level 25–100 MW y^{-1}. This may still come about, eventually — but meanwhile the MCFC does not look outclassed.

As these numbers show, in large systems the cost of the balance-of-plant (peripherals) is as important as the fuel cell. Therefore, simplification and cost reduction of the fuel cell system as a whole have become the focus of attention in MCFC, SOFC as well as PEMFC development. A second consequence is the intense public attention for microfuel cells (of up to 500 W capacity per module). Thus, for example, small PEMFC operating on hydrogen or a DMFC operating on methanol directly, are now considered prime candidates for rapid commercialization, albeit initially in niche applications.

Perhaps the current situation in fuel cell development can be characterized as follows. No particular type of fuel cell has emerged as an all-around favorite. There are only favorite types of fuel cell for particular applications. And all of the fuel cell types are still too expensive compared to competing power generation technology. But they can, and do, take advantage of niche applications and of their capability to accept a wide range of fuels. Especially the high-temperature fuel cells have this advantage. Finally, for a much more rapid and widespread application of fuel cells in large-scale power generation it is necessary to "level the playing field", that is, to take into account externalities (environment and health, supply security) in the electric power price. But this requires political agreement on a national and global scale.

2. Power density aspects

As Fig. 1 shows for the various types of fuel cell, the useful range of voltage under load, approximately 0.6–0.9 V, is not much dependent on the operating temperature and therefore the type of fuel cell. This is unexpected in view of the dependence of ideal (thermodynamic) voltage on temperature, also shown in Fig. 1, which also indicates how this depends on fuel and oxidant utilization. The high-temperature fuel cells (the MCFC, the intermediate-temperature SOFC (ITSOFC), and the classical (tubular) SOFC) operate closer to their ideal potential due to more rapid kinetics and smaller ohmic resistance compared to the "low-temperature" fuel cells (PAFC, AFC, PEMFC, DMFC). Their electrical efficiency is therefore higher.

Also indicated in the figure is the power density range, which is important because it has a major impact on capital cost. The high power density of the PEMFC, and especially of the ITSOFC, explains the commercial promise seen in these types of fuel cell. Note that the maximum power density of a fuel cell is produced at about half the ideal voltage at zero utilization. (This assumes a linear or quasi-linear current–voltage curve, which holds for most fuel cells within normal limits of fuel and oxidant utilization.) The PEMFC and ITSOFC, at the upper limit

of their power density range in Fig. 1, are close to the maximum power condition.

The power density of the MCFC is significantly below that of the competitors above mentioned, including the tubular SOFC. From the cost viewpoint this is a major issue for the MCFC. Fig. 1 makes clear that the MCFC has the potential for much higher power density than that achieved at present. With internal reforming, and operating at 110–160 mA cm^{-2} the MCFC up to now generates 0.15 W cm^{-2} (shown as lower limit in Fig. 1). Improvement in power density has been demonstrated by Japanese researchers (CRIEPI-IHI), who obtained close to 0.25 W cm^{-2} (shown as upper limit in Fig. 1) by operating at 0.3 A cm^{-2} under 0.7 MPa pressure (see, for example, [1], Table 2). However, in their systematic experiments on pressurized stacks the maximum possible power density was not reached yet, so power densities of up to 0.5 W cm^{-2} should not be impossible, in pressurized operation. However, the necessary lifetime at this current level must still be demonstrated.

Since electrode polarization, especially at the cathode, is a major loss factor, we have tried in recent modeling at IIT Chicago to estimate the conditions of cathode and anode structure under which maximum power density may be reached. An agglomerate model was used for each of the two porous electrodes in combination with a stochastic structure model [2,3]. The cathode and anode structure are each characterized by two dimensionless numbers K_1 and K_2 expressing, respectively, diffusion resistance to kinetic resistance, and ohmic resistance to diffusion resistance within the electrodes. These numbers depend on properties of the electrolyte and electrode materials, as well as the porous structure characteristics. For the state-of-the art anode K_1 and K_2 are both approximately 33, and for the cathode 3 and 0.02, respectively.

The results (Fig. 2 is an example) show that in order to maximize power density one needs to increase the agglomerate radius as well as the internal area of the agglomerates. At the same time, maximum power density requires minimizing the thickness. With state-of-the-art electrodes and standard gas com-

positions the maximum power density achievable in atmospheric operation is 0.17 W cm^{-2} at 0.4 A cm^{-2}. However, three times this value could be achieved at double the current density. This would require a cathode structure with a 20 times higher internal area of the agglomerates, and an anode with 30 times higher agglomerate area, while keeping the same agglomerate radius and electrode thickness. Such an internal area would be comparable in magnitude to that of the PAFC and PEMFC porous electrodes operating at 190 and 80–110 °C, respectively. Obviously, the state-of-the-art MCFC electrode materials (nickel powder with Cr or Al additive for the anode, and lithiated nickel oxide for the cathode), even if they would have initially such a high-internal-area, would probably not be capable of sustaining such a high-internal-area structure over tens of thousands of hours.

Therefore, the challenge of achieving high power density depends on finding stable high-internal-area structures. This requires in the first place a deeper understanding of the mechanisms of structure change (coarsening and/or dissolution/deposition). It ties the power density issue to the lifetime issue.

3. Lifetime aspects

The most significant advances in MCFC performance have been made in lifetime (durability), which about 15 years ago was still considered fatally short and difficult to control. Limited lifetime is mainly caused by the corrosive and difficult-to-immobilize electrolyte, as well as the relatively unstable nickel oxide cathode. During the last 10 years, the lifetime of stacks has been stretched from at most a few months to as long as 2 years, even under pressurized conditions. Fig. 3 gives an impression of this advance, accomplished by thorough analysis of the causes of corrosion and dissolution of MCFC components and electrode structures (see, for example [4]).

Although early hopes for breakthrough advances due to novel materials were high, the important advances shown in Fig. 3 are actually the result of incremental improvements. Some of these improvements, though the term "incremental" sounds pejorative, are not minor. For example, optimization of
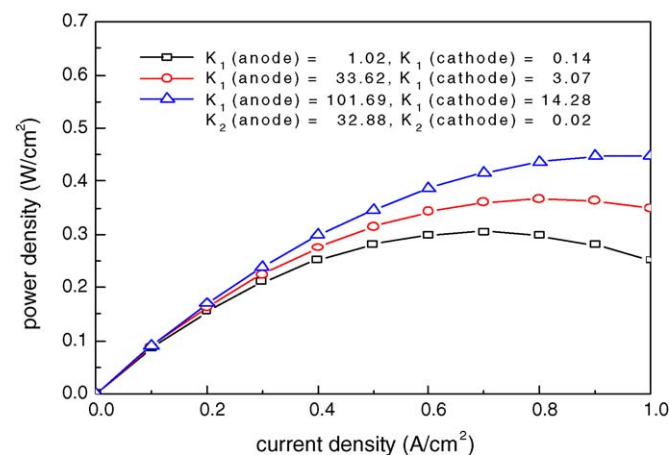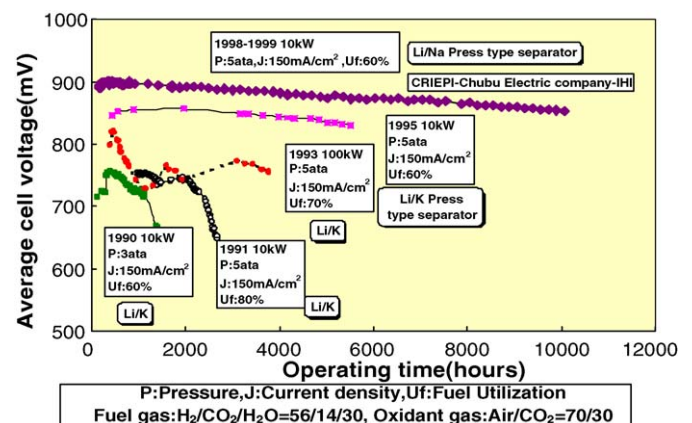

Fig. 2. Effect of electrode structure on power density in atmospheric operation. Structure parameters and properties are combined in dimensionless numbers K_1 and K_2 expressing, respectively, diffusion resistance to kinetic resistance, and ohmic resistance to diffusion resistance within the electrodes (from [2]).

Fig. 3. Lifetime improvement of MCFC (courtesy CRIEPI, Yokosuka, Japan, 2001).

electrolyte composition (Li^+/Na^+/K^+ balance and alkaline-earth cation addition) was initially applied in isolation, i.e., considering electrolyte properties only (such as conductivity, basicity, oxygen solubility, oxygen reduction kinetics). But it has become clear that electrolyte composition is really a system issue. To realize maximum performance at the cell level, electrode materials and structures had to be modified or replaced as well. At the stack level, when a stack has external manifolding of the gas flow, electrolyte movement between cells can occur due to the different mobilities of the cations. Therefore, a change in electrolyte composition must be such as to minimize or compensate this. Another example is the corrosion of stainless steel components, which is appreciably dependent on melt chemistry. The formation sequence and the thickening of passive layers on austenitic stainless steels occurs differently in the more basic Li–Na eutectic than in the standard Li–K eutectic electrolyte.

Lifetime improvements necessitate a system-based approach. For that reason, they are also design-specific. One can nevertheless identify generic areas of fundamental research which would greatly help to achieve the combination of greater lifetime at higher power density.

4. Directions for fundamental research for MCFC

When we consider the present state of MCFC technology and search for "missing links" with our fundamental understanding of its functioning, serious deficiencies are evident in certain areas. These deficiencies must be addressed since improved understanding is essential for long-term progress. They can be summarized as follows:

(1) Wetting of materials by carbonate melts and how it depends on material properties, melt chemistry and polarization. A good systematic beginning has been made (see, for example, [5,6]). But much work remains to be done, and a connection with molecular understanding and modeling needs to be made.
(2) Kinetics of oxygen reduction at a variety of materials (metals as well as oxide semi-conductors) and how these kinetics depend on material properties, melt chemistry and polarization. Amazingly, after more than 20 years of basic electrochemical study, we can assess kinetics but are still uncertain about reaction mechanisms, except that they are complex and depend strongly on melt chemistry and gas composition. One factor that inhibits progress is the severe limitation in spectroscopic access to the electrode and corrosion reactions. But another factor is the scarcity of attempts to model the carbonate melt and its interface with metals and oxides on a molecular scale, and to understand the chemistry of faradaic reactions such as oxygen reduction at various temperature levels.
(3) Corrosion of alloys (with passive layer formation), and dissolution/deposition mechanisms, especially applied to porous or layered composite substrates. This area of research suffers from not having a "fundamental research" image since it is so closely tied to practical needs. But its

complexity makes it a challenge to devise new fundamental approaches.

5. Direct carbon fuel cell

After 30 years of intensive development the MCFC has reached a technically mature state. This has motivated some researchers to look beyond the classical fuel gases, that is, natural gas or low-Btu coal gas. The idea of using the simplest of possible fossil fuels – carbon – is very old, dating back more than a century when molten hydroxide was used by Jaques and others as electrolyte in a coal-fed fuel cell with iron cathode. (See [7] for details about this fuel cell and other early developments here referred to.) The hydroxide melt turned to carbonate and the performance deteriorated, cutting short the life of the cell. For this reason, Broers and Ketelaar, now 50 years ago, adopted pure carbonate as a logical extension of the earlier explorations, and thereby pioneered the MCFC as we know it now.

Since then, direct anodic oxidation of carbon in carbonate melt has practically been abandoned, except for occasional explorations. The main reason for poor performance was perceived to be the leaching of impurities in carbon (and especially in coal), leading to contamination of the melt. Also, the desirable four-electron oxidation of C to CO_2 (if achieved at all, which is not easy to confirm experimentally) is always under threat of being reduced to a two-electron process due to the powerful driving force for CO formation by the Boudouard reaction of C with CO_2. Recently, however, the electrochemistry of anodic C oxidation has been revisited in a systematic exploration of the optimal conditions for its viability by Cooper and co-workers at LLNL [8,9].

Two significant advances were achieved in this work:

(1) The polarization of anodic oxidation was determined for various types of carbon and it was found to be overall relatively small, at least for carbons of a favorable molecular structure (turbostratic grapheme-based).
(2) The anodic oxidation of carbon to CO_2 was shown to take place at high current efficiency, and a mechanism for this four-electron process was proposed that significantly helps optimal design.

The above authors also constructed a viable bench-scale fuel cell, and designed a scaled-up system for the purpose of economic evaluation. But achieving adequate power density remains a challenge (see Fig. 4). It will require a simultaneous optimization of cell (and stack) design for both maximum current density and minimal back-reaction to CO. Under less stringent conditions the DCFC has the important advantage of complete utilization at constant voltage, which makes it suitable as a high-temperature fuel battery (primary battery).

6. Direct oxidation of CO and CH_4 — connection with low-temperature SOFC and hybrid MS/SOFC

The DCFC research is related indirectly to anodic CO oxidation to CO_2, since this could be part of a possible mechanism
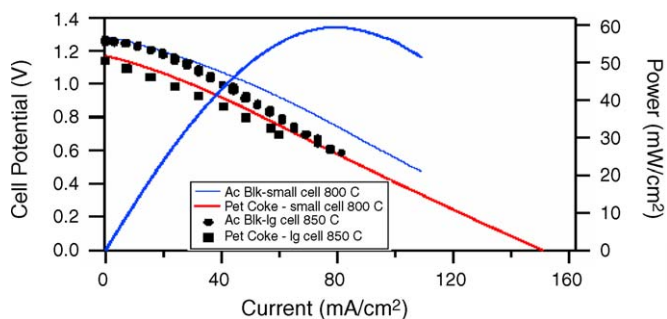
Fig. 4. Performance of DCFC cells. Courtesy of Cooper (LLNL, Livermore, USA).

producing CO_2 by anodic C oxidation (against thermodynamic trends). The rate of anodic CO oxidation is an issue that has remained unresolved in MCFC research. This is due to the inability to distinguish, in the presence of hydrogen, between indirect oxidation (by water gas shift equilibration) and direct anodic oxidation. Direct oxidation of CO has long been assumed to be very slow compared to that of hydrogen, but there is no clear experimental evidence. In the MCFC, dry CO tends to deposit carbon.

The direct anodic oxidation of CO has been studied intensively in work by Swedish researchers [10]. CO is a major component of alternative fuel gases such as biomass gas and other low-Btu gases, which are naturally compatible with MCFC operation. Overall, this work seems to indicate a larger role for direct CO oxidation than previously assumed, although the rate of direct CO oxidation is still 20 times smaller than the exchange current density of hydrogen [11].

As was the case for CO, direct anodic oxidation of CH_4 was initially explored by MCFC researchers. This led to the conclusion that it probably occurs at negligibly small rate under MCFC conditions. It was believed that this is due primarily to the very small solubility of CH_4 in molten carbonate. As a result, primary emphasis in MCFC R&D went to CH_4 (and hydrocarbon) internal reforming, and this effort has been largely successful. Direct (in-cell) and indirect (in-stack) internal reforming are now used in MCFC system design.

Recent SOFC research aimed at an intermediate-temperature (600–800 °C) or low-temperature (<600 °C) SOFC (ITSOFC and LTSOFC, respectively) has revived interest in the "direct oxidation" of CH_4. It has been shown that LTSOFC cells using YSZ electrolyte and Ni/YSZ anode are able to operate on nearly dry methane [12], and that ITSOFC cells using YSZ or ceria/YSZ electrolyte and Cu-based anodes are able to operate on dry methane [13]. Note that Cu is a poor catalyst for CH_4 pyrolysis, which is the primary reaction expected to occur, especially at 600–800 °C.

These findings are relevant for molten-salt fuel cell technology. For the state-of-the-art MCFC they suggest that Cu as an anode material deserves a second look in spite of less favorable H_2 oxidation kinetics. On the other hand, they provide a strong argument for lowering the operating temperature of a "high-temperature" carbonate fuel cell, by any means possible. This would imply a drastic (not incremental) change in the state-of-

the-art MCFC since the traditional materials (alkali carbonate eutectic and non-noble metal cathodes) do not allow operation below 550–600 °C.

Especially interesting, therefore, is the recent work of Zhu et al. (for example, [14]. They reported high ionic conductivity ($0.01–1\,S\,cm^{-1}$ in the range 300–600 °C) for a micro-composite electrolyte consisting of ceria and Li–Na carbonate. (For microcomposite solid electrolyte of ceria and lanthanum oxide similarly high conductivities were reported.) A fuel cell using the composite electrolyte of molten-salt/solid electrolyte type, as well as electrodes of similar non-specified composites, was reportedly capable of producing $0.25\,W\,cm^{-2}$ at 400 °C, on hydrogen and oxygen. The unusual conductivity and electrode activity at such a low temperature was ascribed to the composite structure consisting of nano-to-microscale particles. High defect concentrations at the surface of nanoparticles of the host oxide were assumed to cause a large activity for gas-solid catalysis as well as a high ionic conductivity. At the inter-phase boundaries with the carbonate (or lanthanum oxide) a high surface conductivity would result, which then would establish a continuous current path, basically along grain boundaries.

Although this explanation is partial, and part of these results are reputed to be poorly reproducible, the main claims about high effective conductivity of microcomposites have been confirmed in recent German work [15]. This work also provides an explanation in the framework of solid-state physics. Sharp discontinuities in the σT versus T graphs were observed for many, but not all, microcomposites of solid-oxide proton (or oxide) conductors and inorganic compounds such as carbonates, hydroxides, and chlorides. Such discontinuities in conduction (at transition temperatures varying from 400 to 520 °C depending on the inorganic compound as well as the solid ionic conductor)) were ascribed to a phase transition from superionic conduction (below the transition temperature) to protonic or oxide super-conduction (above the transition temperature).

7. Conclusions — a role for nanotechnology?

The recent work on hybrid microcomposite conductors raises the question whether nanotechnology has anything to contribute to molten-salt fuel cells, and high-temperature fuel cells in general. The question would be generically answered with "no", or "highly doubtful" by many, which is understandable because thermodynamic driving forces tend to be so spectacularly dominant at temperatures exceeding 300–400 °C.

Nevertheless, there is reason to consider the question with an open mind. It introduces a radically new idea into the MCFC technology. This technology, and also – to a lesser degree – SOFC technology, have become more or less frozen in the choice of materials and the kind of design these materials dictate. In some ways this trend has stifled creativity. The concept of microcomposite structures in a fuel cell operating at the limits of combined molten-salt and solid ionic conduction may perhaps lead to a breakthrough in performance, once the condition for reproducibility has been understood. On the other hand, it may lead to a limited range of application. It may cause major

changes in the state-of-the-art MCFC, or it may generate a new and possibly competing technology.

In practice, the first concern is to establish the viability of microcomposite electrodes for the long term, under load. From a fundamental viewpoint, one would also need to understand why a higher-than-expected conductivity is observed for some combinations of solid ion conductors and inorganic compounds and not for others, as mentioned above. Similarly, the electrodes based on microcomposite structure pose another set of challenges to understanding and design.

Even if this novel idea does not result in a new lower-temperature molten-salt technology, it may still lead to new fundamental research, in addition to areas described above (Section 5). This may benefit the wider application of molten-salt fuel cells.

Acknowledgments

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