

Compact mixed-reactant fuel cells

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Abstract

The compact mixed-reactant (CMR) fuel cell is an important new “platform” approach to the design and operation of all types of fuel cell stacks. Amongst several other advantages, CMR has the potential to reduce polymer electrolyte membrane (PEM) stack component costs by around a third and to raise volumetric power densities by an order of magnitude.

Mixed-reactant fuel cells, in which the fuel and oxidant within a cell are allowed to mix, rely upon the selectivity of anode and cathode electrocatalysts to separate the electrochemical oxidation of fuel and reduction of oxidant. A comprehensive review of the 50-year history of mixed-reactant literature has demonstrated that such systems can perform as well as and, in some circumstances, much better than conventional fuel cells.

The significant innovation that Generics has introduced to this field is to combine the concept of mixed-reactant fuel cells with that of a fully porous membrane electrode assembly (MEA) structure. Passing a fuel–oxidant mixture through a stack of porous cells allows the conventional bipolar flow-field plates required in many fuel cell designs to be eliminated. In a conventional PEM stack, for example, the bipolar carbon flow-field plates may block up to half of the active cell area and account for up to 90% of the volume of the stack and of the order of one-third of the materials costs. In addition to all the advantages of mixed-reactant systems, the “flow-through” mode, embodied in Generics’ CMR approach, significantly enhances mass-transport of reactants to the electrodes and can reduce reactant pressure drops across the stack. Redesigning fuel cells to operate in a CMR mode with selective electrodes offers the attractive prospect of much reduced stack costs and significantly higher stack power densities for all types of fuel cell.

Initial modeling and proof of principle experiments using an alkaline system have confirmed the validity of the CMR approach and the potential for substantial performance improvements. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Mixed-reactant; Fuel–air mixture; Methanol; Sodium borohydride; Fuel cell

1. Introduction

Conventional fuel cells operate using active but often non-selective electrocatalysts and rely upon a strict segregation of fuel and oxidant to prevent parasitic chemical reactions at the electrodes. Mixed-reactant fuel cells, which have been known for around half a century, rely upon the selectivity of anode and cathode electrocatalysts to separate the electrochemical oxidation of fuel and reduction of oxidant. Without a need for physical separation of fuel and oxidant, there is no longer any need for gas-tight structures within the stack and considerable relaxation of sealing, manifolding and reactant delivery structures is possible.

The compact mixed-reactant (CMR) fuel cell is an entirely new concept in which a mixture of fuel and oxidant is flowed through a fully porous anode–electrolyte–cathode

structure. This structure may be a single-cell, series stack or parallel stack and may be in planar, tubular or other geometry. In principle, a CMR cell may be based on polymer, alkaline, phosphoric acid, molten carbonate, solid oxide or any other type of fuel cell chemistry. Whatever the specific geometry or chemistry, for this type of cell to work effectively, the anode and cathode electrocatalysts must be substantially selective—i.e. the anode should be active toward fuel oxidation and tolerant to oxygen, while the cathode should be active toward oxygen reduction and tolerant to fuel.

Selectivity in the electrocatalysts for a mixed-reactant or a CMR fuel cell is needed to minimise mixed potentials at the electrodes which otherwise will reduce the available cell voltage and compromise the efficiency of conversion to electricity. Loss of efficiency reflects the extent of the “parasitic” direct reaction of fuel and oxidant to produce heat rather than electric current. This is directly analogous to the problem of methanol cross-over from the anode compartment to cathode compartment in conventional direct-methanol fuel cells. A range of partially and substantially

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selective catalysts have become available in recent years, largely as a result of the continuing effort to develop more effective catalysts for direct-methanol fuel cells.

2. Significance of the compact mixed-reactant fuel cell

Two key advantages of operating any fuel cell stack in the flow-through CMR mode are as follows:

- flow-field structures can be eliminated from within the stack;
- mass-transport of reactants to electrodes is much higher than in conventional or mixed-reactant stacks.

These key advantages are supported by those more generally of mixed-reactant systems, which include: reduced manifolding and sealing; single feed supply to one side of fuel cell only; reduced quantities of materials and component count; lower tolerance component manufacturing and easier stack assembly.

The consequence of eliminating the bipolar flow-field plates is a huge reduction in volume and cost of a fuel cell stack. For a polymer electrolyte membrane (PEM) stack this volume reduction could be as high as 80–90%. In several semi-commercial designs of planar solid oxide fuel cell, the ceramic or metal bipolar interconnector is the single most expensive component. Removing it could reduce the stack cost by around 30–60%. Increasing the mass-transport of reactants to the electrodes has the immediate effect of increasing cell current density. The reduction in diffusion boundary layers between reactants and catalyst particles may also reduce the amount of catalyst required per kilowatt of power generated by the cell. The combined effects of increased mass-transport and smaller stack volume should be a large increase in volumetric power density for the stack and a reduction in the power required to pump reactants through the stack.

An example of the potential volumetric power density that a CMR stack may deliver is provided by an experimental programme underway at Generics. In this programme, the performance of a small DMFC stack with a mixed vapour feed of humidified methanol and air will be tested in flow-through mode. The stack is designed to consist of a series of closely spaced fully porous MEAs, with each cell interconnected electrically by a thin and porous carbon gas diffusion layer (GDL) and no flow-field plate. Assuming that each GDL and MEA sheet is around 100 μm thick then a cell pitch of around 50 cells cm^{-1} should be readily achievable. (This compares with a “conventional” cell pitch of around 2–5 cells cm^{-1} .) Using existing selective cathode materials, we anticipate that it should be possible to achieve at least 50 mA cm^{-2} at a cell voltage of 0.4 V in CMR mode. If this moderate cell performance can be achieved at this cell pitch, the stack should achieve a volumetric power density of 1000 W l^{-1} , approximately equivalent to that of a conventional hydrogen-fuelled PEM stack.

With the lower fuel efficiencies resulting from today’s generally poorly selective electrocatalysts in CMR mode, one challenge associated with very high stack densities will be cooling. Although cooling is readily achieved in all-liquid fuel cells, this issue may limit the maximum power density of gas-phase CMR systems until improved electrocatalysts are developed specifically for them.

3. History of mixed-reactant fuel cells

As has been observed many times elsewhere, the history of the fuel cell goes back more than one and a half centuries. In that period many individuals and organisations have devoted considerable efforts and resources to the invention, development and demonstration of various fuel cell technologies. One such technology that has been investigated for alkaline, solid oxide, polymer and direct-methanol fuel cells is the “mixed-reactant” or “single-chamber” fuel cell [1–33].

Starting in the 1950s, when nuclear fission plants were under intense development, fuel cell engineers examined the possibility of radiolytic splitting of water into hydrogen and oxygen followed by electrochemical recombination of the gas mixture to generate electricity. Fuel cell stack geometries with alkaline electrolytes (anion membrane or KOH) were tested by Grüneberg and others of Varta and Siemens in which the oxygen in a stoichiometric $\text{H}_2 + 0.5 \text{O}_2$ gas mixture was first depleted to below the flammability limit at a selective cathode (e.g. C, Ag, Au)—i.e. a cathode capable of reducing oxygen molecules to oxygen ions but incapable of oxidising hydrogen gas to ions [1]. To complete the cell reaction, the depleted gas mixture was subsequently exposed to an anode electrocatalyst (e.g. Pt, Pd) that promoted hydrogen oxidation. In a later variant, in which the same gas mixture was delivered to each electrode, using a silvered nickel cathode and Pd–Pt anode, Goebel et al. [2], operated a liquid alkaline fuel cell at room temperature on a 9% $\text{O}_2 + 91\% \text{H}_2$ oxyhydrogen gas mixture. This cell delivered an open circuit voltage (OCV) of 1.0 V and a current density of 4 mA cm^{-2} at 0.4 V.

Around the same time as Grüneberg and Goebel, in 1961, Grimes et al. [3] of Allis Chalmers built and operated a 600 W direct-methanol mixed-reactant alkaline fuel cell. A series-connected 40-cell stack of 25 cm \times 25 cm solid bipolar Pt–Ni–Ag electrodes was supplied with a liquid reactant mixture consisting of hydrogen peroxide (0.1–1 wt.%) and methanol (2–10 wt.%) in a 0.5–7 M potassium hydroxide solution and delivered up to 40 A at 15 V. In single-cell tests using a solid anion membrane as electrolyte, an OCV of 0.41 V was measured in the reactant mixture compared to 0.81 V when methanol and hydrogen peroxide were supplied separately in KOH solution to the Pt anode and Ag cathode. Analysis of reaction products determined that the net reaction in the cell was the oxidation of methanol to potassium methanate (formate), possibly either by direct

electrochemical reaction for which the theoretical cell voltage is 1.88 V, or via disproportionation of a chemically generated methanal (formaldehyde) intermediate for which the EMF would be 0.94 V. Quantitative comparison of the reaction products with the charge passed by the cell indicated that significant direct chemical reaction occurred between the reactants (as opposed to electrochemical oxidation). Further tests indicated that this chemical short circuiting was primarily catalysed at the platinum electrode. Although not a particularly fuel efficient cell, the Grimes' device was clearly a powerful and early demonstration of the feasibility of liquid-phase mixed-reactant fuel cells.

Also in 1961, Eyraud described another gas-phase mixed oxygen–hydrogen device in which a micro-porous alumina support flooded with condensed moisture from the humid gas mixture acted as a film electrolyte [4]. In this case the Ni–Al₂O₃–Pd cell was operated as a sensor with OCV varying from –0.35 to +0.6 V, depending upon gas composition (no power was drawn from this cell). Then, in 1965, extending Eyraud's work on film electrolytes, van Gool, described for the first time, a further variant of the mixed-reactant fuel cell, the "surface-migration" cell [5]. In this geometry, two closely spaced selective electrodes (anode and cathode) are positioned on the same side of an insulating substrate with a film electrolyte between them. While such a geometry could be operated with separate feeds of hydrogen and oxygen, van Gool suggested that the close electrode spacing (~1 μm) required for a film electrolyte would make gas separation impracticable. For the selective anode electrocatalyst he suggested that a metal with a stable or partly stable hydride and unstable oxide (e.g. Pt, Pd, Ir) would be an appropriate starting point for experimentation; for the selective cathode, a metal, such as silver with unstable hydride and stable oxide. van Gool also suggested that the metals W, Ni and Fe which catalyse the dissociation of methane and ethane below ~200 °C, might work as effective anodes in a mixed-reactant system based on hydrocarbon fuels, in which oxygen or oxygen ions are available to mitigate carbonisation of the anode. No experimental work was reported by van Gool.

There was a gap of 14 years before Louis et al. [6] of United Technologies tested a single-cell variant of van Gool's [5] mixed-reactant "surface-migration" cell. In the UTC approach, a supported thin-film (3 μm) alumina electrolyte was employed, along with closely spaced (300–400 μm gap) supported Pt anode and SrRuO₃ cathode. Each electrode was 5 μm thick and 2.0 cm × 0.5 cm in area. With a single humidified mixed gas feed of 4% O₂, 4% H₂ in nitrogen, an OCV of 0.67 V was obtained at room temperature and, at peak power, a current density of 0.82 μA cm⁻² at 0.39 V. UTC went on to describe a surface strip-cell geometry in which multiple pairs of surface electrodes are interconnected electrically in series and in which several of such layers are connected in parallel. Alternative electrolyte and selective anode and cathode electrocatalysts (e.g. zirconia, LaCo_{0.5}Ru_{0.5}O₃, LaMnO₃) were also suggested.

In 1990, Moseley and Williams [7] of AEA Technology described a similar room temperature Pt-oxide–Au surface-migration cell, which they had tested as a sensor in various gas mixtures. Using a porous metal (W, Sn) oxide as substrate for the sputtered metal electrodes and for condensation of an aqueous film electrolyte, they discovered that this cell generated an OCV of up to 0.5 V in humid air alone. Adding small amounts (up to approximately 1%) reducing (fuel) gases, such as H₂, CO, NH₃ or EtOH to the gas mixture, they found that the OCV of the cell increased approximately as the log of the concentration of the reducing gas. The authors reasoned that the OCV response in ambient air was a result of the different mixed potentials established by oxygen reduction and metal oxidation at the respective gold and platinum electrodes. Introduction of an additional fuel gas, they believed, mainly affected the mixed potential at the Pt electrode.

Also in 1990 (although with a Patent priority in 1988), Dyer, who was actually working on hydride batteries at Bell Communications Research, described a quartz-supported thin-film mixed-reactant fuel cell that operated with active but apparently non-selective electrodes [8–11]. As with the systems described by Eyraud et al. [4], van Gool [5] and Louis et al. [6], Dyer used a hydrated alumina film as an electrolyte (0.5 μm). In his system, however, the electrodes, which are positioned on either side of the alumina film, can be identical and are either Pt or Pd. Only one electrode of the thin-film cell is exposed to the fuel (H₂, CH₄, MeOH)-oxidant (air, O₂) mixture, while the other side is supported by an impermeable substrate. Dyer found, in his initial experiments with hydrogen–air gas mixtures, that the outer or first Pt electrode was negative (i.e. was the anode), while the inner Pt electrode was positive (cathode). OCV varied over a range of ~0.2–1.1 V, depending upon gas composition, with OCV > 0.95 V when the gas mixture consisted of at least 50% H₂. Perhaps the most important factor contributing to the magnitude and polarity of the observed OCV is that the inner Pt electrode was treated in boiling water to convert an initial < 50 nm coating of Al metal to boehmite phase alumina. It is likely that in this preparation process the Pt surface itself was oxidised. Compared to Pt metal, Pt-oxide has been reported to be a reasonably selective cathode, i.e. promoting O₂ reduction at the expense of H₂ oxidation [12]. A secondary contribution to OCV may be from the differential oxygen reduction/electrode oxidation reactions occurring in the presence of a hydrous electrolyte film (Moseley and Williams [7] observed potentials up to 0.5 V). A third but possibly weaker contributor to the observed behaviour of Dyer's cell may be that a concentration gradient in the local gas mixture is established either by gettering of hydrogen at the exposed electrode or by differential diffusion rates between oxygen and hydrogen in the pinhole-free alumina layer [9,13]. An alternative explanation, based on the relative ability of the two electrodes to catalyse the formation of hydrogen peroxide (the inner electrode being more active), was given by Ellgen, of

Kerr-McGee, which provided the untested basis for a 1991 Patent which claimed a Pt–Pd alloy as a preferred cathode, simultaneously active toward chemical formation and electrochemical reduction of H_2O_2 , and an anode that is inhibited toward peroxide formation but active toward hydrogen oxidation [14].

Dyer was able to reverse the polarity of his cell by changing the outer electrode to Ni. This reflects Grüneberg's original mixed-reactant cell of the 1950s which featured selective depletion of oxygen as the gas-phase mixture was exposed first to a hydrogen-inert cathode and then to a hydrogen-active anode [1]. Dyer was also able to draw $\sim 1\text{--}5 \text{ mW cm}^{-2}$ from his $\text{H}_2\text{--O}_2$ Pt–Pt cell with cell voltage falling by $\sim 0.2\text{--}0.3 \text{ V}$ per decade of current in the range $0.1\text{--}3.0 \text{ mA cm}^{-2}$. He proposed that his thin-film fuel cell would be particularly suitable as an integrated power source in planar electronic circuits and, if deposited on a flexible substrate, could also be packaged in a compact stack form (e.g. spirally wound) to replace conventional batteries, potentially with the fuel-oxidiser mixture being supplied in liquid form [10,15]. An efficiency improvement to Dyer's cell was suggested by Taylor (also of Bell Communications), involving patterning the outer electrode and coating it with a fuel-permeable, oxygen-impermeable barrier to increase anode selectivity to fuel and the permeability of the cell to oxygen [16]. A later (Motorola, 1996) improvement to the general mixed-reactant cell for battery-type applications included an absorbent material to eliminate water discharge [17].

In 1990, approximately concurrent with Dyer's report [9], Wang et al. [18] of GTE Laboratories, filed Patents on a two-interconnected-chamber mixed-reactant Pt–YSZ–PT SOFC. Although a mixed-reactant yttria-stabilised zirconia (YSZ) electrolyte cell was described previously in Louis et al. [6] Patent, this was the first time such an elevated-temperature cell had been demonstrated in practice. The mechanism of operation of Wang's cell is not entirely clear, but seems to be via either differential flow rates of the methane–air mixture to each electrode or via an initial electrical pulse (in the range of several millivolts to volts) that may establish one Pt electrode as anode and the other as cathode. It is stated that the device will operate as a fuel cell only up to 450°C and can be operated on any reducing gas and with alternative electrolytes and with different electrodes (e.g. Pt–Au). At 350°C , Wang's Pt–YSZ–Pt cell provided an OCV of 0.95 V and a current of $70 \mu\text{A}$ at 0.65 V in a methane (10%)–air mixture. A second embodiment of the device, which was reported to give much improved performance at up to 600°C , appears to supply the fuel (ethane or methane)–air mixture to only one side of the cell, with the other side possibly being exposed to air.

Continuing the development of mixed-reactant SOFCs, in 1993, Hibino and Iwahara reported a high-temperature "single-chamber" solid oxide fuel cell operating on a methane–air mixture [19,20]. At 950°C , Hibino's Ni–YSZ–YSZ–Au single-cell delivered an OCV of 0.35 V

and, at peak power, 15 mA cm^{-2} at 0.16 V in a 2:1 $\text{CH}_4\text{:O}_2$ mixture. GC analysis of the off-gas from each electrode showed that the Ni–YSZ anode was an effective catalyst for the partial oxidation of methane to hydrogen and carbon monoxide, while the gold cathode was a much less effective catalyst for partial oxidation. The measured gas compositions at each electrode corresponded reasonably well with the Nernstian partial pressure of oxygen at each electrode, calculated from the respective half-cell potentials (-0.9 and -0.2 V , Pt–YSZ reference). This, combined with OCV = 0 V measured when the cell was supplied with air, N_2 or H_2 alone or when both electrodes were identical, led Hibino to conclude that cell EMF is largely due to the local oxygen concentration gradient generated by the difference in catalytic activity (toward partial oxidation of methane) between the two electrodes. Hibino also reasoned that the high cathodic overpotential (0.5 V at 10 mA cm^{-2}), due to gold's poor activity toward oxygen adsorption, diffusion and reduction, could be improved by replacing the oxygen electrolyte with a proton conductor. In subsequent experiments, Hibino was able to increase the peak specific power of his mixed-reactant SOFC from $\sim 2 \text{ mW cm}^{-2}$ (0.5 mm YSZ electrolyte) to 166 mW cm^{-2} (0.5 mm $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_3$) [21,22]. In this latter system, at 950°C , a Pt anode and Au cathode were used, reducing both electrode overpotentials to $<50 \text{ mV}$ at $\sim 200 \text{ mA cm}^{-2}$ and giving an OCV of 0.8 V and current density of 400 mA cm^{-2} at 0.42 V . It was also found that performance of an Au–YSZ–Pt mixed-reactant cell could be significantly improved by surface doping of the YSZ with Pr to render it electronically conducting [23].

Separate measurements by Gödickemeier in 1997 at ETH-Zurich [24] on a Au–TZP–Pt (TZP = $0.3 \text{ mol}\%$ YSZ) single-cell, over a range of methane–air compositions, indicated an equilibrium oxygen partial pressure, $p(\text{O}_2)^{\text{eq}}$, at the Pt anode of 10^{-17} atm and a non-equilibrium $p(\text{O}_2)^{\text{neq}}$ at the Au cathode of 0.18 atm at 700°C in a 3:2 methane:air ratio. OCV for this cell was 0.8 V (corresponding with the Nernstian voltage expected from the measured $p(\text{O}_2)$ values), with a current density of $\sim 10 \text{ mA cm}^{-2}$ at 0.6 V and $\sim 30 \text{ mA cm}^{-2}$ at 0.2 V . These results support Hibino's results and analysis of mixed-reactant SOFCs.

A theoretical analysis of Hibino's and Iwahara [19] and Dyer's [9] results of single fuel cells operating in fuel–air gas mixtures was given by Riess et al. [25]. With a uniform oxygen partial pressure supplied to each electrode, Riess started with the proposition that the asymmetry required to drive an ionic current through the electrolyte must originate from a difference in the catalytic properties of the two electrodes. He showed that an ideal mixed-reactant cell will provide identical OCV and $I\text{--}V$ behaviour to that of a conventional fuel cell when one electrode is reversible towards oxygen adsorption and completely inert to fuel, and the other exhibits reversible fuel adsorption and is completely inert to oxygen. He argued that the actual OCV measured in Hibino's cell was lower than the theoretical value because imperfect catalyst selectivity promoted

direct fuel-oxygen reaction which reduced the chemical potential across the electrolyte. One additional conclusion of Riess' analysis is that the electrolyte does not need to be impervious to fuel oxidant or reaction products.

Logically, Hibino recently tested the practicality of a conventional Ni-YSZ-La_{0.8}SrMn_{0.2}O₄ SOFC single-cell in mixed-reactant mode, obtaining an OCV of 0.8 V at 950 °C and at peak power, ~300 mA cm⁻² at 0.4 V with an inlet gas mixture consisting of 19% CH₄, 16% O₂ and 65% N₂ [26,27]. He has also demonstrated that an intermediate-temperature (500 °C) SOFC with 0.15 mm Ce_{0.8}Sm_{0.2}O₂ (SDC) electrolyte (or with other electrolytes), Ni-SDC anode and Sm_{0.5}Sr_{0.5}CoO₃ cathode can operate effectively in "single-chamber" mode when supplied with gas mixtures of methane, ethane, propane or LPG in air [28,29]. In the SDC cell, supplied with an ethane (18%)–air mixture at 500 °C, OCV was ~0.9 V and at peak power, a current density of ~800 mA cm⁻² at ~0.5 V was measured. In all the cases, measurements of electrode off-gas compositions support Hibino's original conclusion (and Riess' later analysis) that cell OCV is determined largely by the oxygen concentration at each electrode which itself is determined by the extent of partial oxidation of the hydrocarbon at each electrode. Hibino uses this as the basis of a Patent [30] on a series-connected surface strip-cell SOFC geometry (exposed to a gas mixture on one side only), similar in many respects to the "surface-migration" cell proposed by van Gool in 1965 [5] and later patented in series-connected form by Louis et al. [6].

In related work at ETH-Zurich, Joerger [31] described a further variant on the strip-cell SOFC geometry. In the ETH design, each side of a zirconia (TZP) electrolyte sheet is coated with a series of alternating and physically separated anode and cathode electrode strips, with each alternated pair interconnected electrically with gold wire. Additionally, the electrodes on the two sides are arranged so that anodes are opposite cathodes and electrically connected anode–cathode pairs are opposite electrically separate cathode–anode pairs. Electrical connection to an eight cell arrangement of this type was made to the outer anode (Pt) and cathode (Au) on one side of the electrolyte (TZP) sheet, giving an OCV of ~4.5 V at 700 °C in a methane–air mixture. The connection geometry suggests that the intention in this design is for oxygen ions to be conducted across the thickness of the TZP electrolyte (i.e. between opposite electrodes), rather than along the surface of the TZP, as would be the case in a "surface-migration" strip-cell (i.e. between adjacent electrically separate electrodes). Clearly both ion conduction paths are possible in such a design—risking ionic short-circuiting—with the preferred path being determined largely by electrode separation distances. Recently, Zhu et al. [32] at RIT-Stockholm proposed an essentially identical geometry that solved the issue of ionic short circuiting by replacing the single zirconia electrolyte layer with a double electrolyte sandwich of YSZ (50 μm)–Al₂O₃ (0.5–1 mm)–YSZ (50 μm). The alumina support acts as a barrier to oxygen

ion transport, so that each side of the series-connected strip-cell design acts purely in a surface-migration mode. Zhu's design also included stacking of many such layers in a manner similar to that proposed previously by Louis et al. [6].

Very recently, researchers from IFC and U. Texas [33] demonstrated the feasibility of a mixed-reactant direct-methanol PEM cell, showing that performance in mixed-reactant mode with selective electrodes could exceed that in conventional mode when identical rates of fuel and oxidant are supplied to anode and cathode, respectively. They also conducted a design study in which the dimensions of a series of mixed-reactant surface strip-cells were optimised. In the single-cell tests, a two-phase reactant mixture of 1 M methanol solution (3 cm³ min⁻¹) and air (3 dm³ min⁻¹) was supplied to both sides of a conventional geometry membrane electrode assembly (MEA) at 80 °C. The 32 cm² MEA was a Nafion-117 electrolyte coated on one side with a hydrophobic Pt–Ru C-black (5 mg cm⁻²) anode, and on the other with iron tetramethoxyphenyl porphyrin (FeTMPP), a methanol-tolerant cathode material. Half-cell experiments were also carried out on these electrodes (with Pt counter electrode) and also on another selective cathode electrocatalyst, Ru–Se–Mo (5 mg cm⁻²). The half-cell measurements demonstrated that, in this system, there was no significant reaction between oxygen and methanol at the anode and that the main effect of the entrained air (or entrained nitrogen) in the mixed-feed was to impede mass-transport of the fuel to the anode at current densities above 100 mA cm⁻². At the cathode, half-cell measurements again showed little significant difference between operation in mixed-reactant mode and conventional mode, a 40 mV drop in OCV being measured for FeTMPP in mixed-reactant mode while a ~20 mV increase in OCV was measured for Ru–Se–Mo.

Cell performance was compared in mixed-reactant mode and in conventional mode (air supplied to cathode; MeOH to anode). For both cathode systems, the OCV (0.5–0.6 V) in mixed-reactant mode was virtually identical to that in conventional mode, while slightly higher current densities were measured for the mixed-reactant systems: at 0.3 V current densities were approximately 12 and 16 mA cm⁻² for the Ru–Se–Mo cathode, and 23 and 33 mA cm⁻² for the FeTMPP cathode, in mixed-reactant and selective modes, respectively. One possible explanation for the slightly higher current densities in mixed-reactant mode could be that methanol crossed-over from the cathode side to the anode side by permeation through the electrolyte membrane (driven by depletion of methanol at the anode). If this is the explanation, it is important to note that it is only possible because in their experiments the IFC and U. Texas team supplied the mixed-reactant cell with twice the amount of methanol (3 cm³ min⁻¹ to both anode and cathode) supplied to the conventional DMFC (3 cm³ min⁻¹ to anode only).

In the mixed-reactant DMFC, one could argue that methanol cross-over offers a performance advantage—quite the opposite to the situation in a conventionally operated PEM

DMFC. In the latter case, methanol leaks constantly from anode compartment to cathode compartment where it reacts at the unselective cathode electrocatalyst (typically Pt), thereby lowering its potential as well as wasting fuel through direct chemical reaction. This has its most significant effect on fuel efficiency (the ratio of electrical energy output of the cell to heat of combustion of fuel entering the cell) when the conventional DMFC cell is being operated at low current densities. The IFC and U. Texas team were able to show that the fuel efficiency of their mixed-reactant DMFC using a selective FeTMPP cathode remained higher than that of a conventional geometry DMFC with non-selective Pt cathode up to a current density of $\sim 100 \text{ mA cm}^{-2}$. Of course, this efficiency improvement would be evident in a conventional DMFC also, if Pt were replaced by FeTMPP. This is one of the primary reasons why selective cathode materials, such as FeTMPP and Ru–Se–Mo were investigated in the first place.

The 50-year history of mixed-reactant fuel cell systems has demonstrated convincingly that they can deliver performance comparable to that of conventional fuel cells, that multiple cells can be stacked in series and that the mechanisms by which they work are well understood in terms of catalyst selectivity and local chemical gradients generated at the electrodes. Moreover, the range of work carried out in this area demonstrates that the mixed-reactant approach is applicable to gaseous and liquid systems, to systems operating over a wide range of temperatures, to alkaline, solid oxide and PEM fuel cell types and, by implication, to all fuel cell types.

The key advantages of mixed-reactant systems identified by the various workers in this field can be summarised as follows:

- more compact designs possible because manifolding simplified;
- surface strip-cell geometry enables series cell connections and exposure to reactant on just one side of structure;
- supported thin-film cell with porous electrolyte and surface electrode enables exposures from just one side;
- higher power densities possible by closer stacking of thin-film and strip-cell geometries;
- lower fabrication costs possible from continuous coating of supported thin-film and strip-cell structures;
- lower cost and more reliable systems because sealing requirements reduced or eliminated.

Key disadvantages of mixed-reactant systems are as follows:

- selective (as well as active) catalysts required to prevent polarisation losses and fuel inefficiencies due to parasitic side reactions;
- fuel cell exhaust may contain a larger proportion of more dilute unreacted fuel than in conventional anode exhaust;
- fuel (non-reacting) dilutes oxidant concentration (or partial pressure) at cathode (Nernst potential very slightly reduced);

- oxidant (non-reacting) dilutes fuel concentration (or partial pressure) at cathode (Nernst potential very slightly reduced).

At their best, with ideally selective and active anode and cathode electrocatalysts, with identical geometries and fuel and oxidant activities, mixed-reactant single-cells should have identical performance to conventional fuel cells. In certain types of cell, for example, where fuel cross-over depresses performance, or where reaction products may depress electrocatalyst activity, it appears possible for mixed-reactant cells to out-perform conventional separate-reactant cells. At present, ideally selective catalysts are not available for fuel cells and those substantially selective electrocatalysts that do exist are not as active as conventional fuel cell electrocatalysts toward either fuel oxidation or oxygen reduction. Although there are presently no significant efforts to develop selective anode or cathode electrocatalysts for mixed-reactant fuel cell systems, there are significant efforts in the fuel cell community to develop methanol-tolerant cathode materials for DMFCs as one means of helping to alleviate the problem of methanol cross-over. These electrocatalysts are also ideal candidates for the cathodes of mixed-reactant DMFCs and are a starting point for a more substantial development effort for catalysts designed to enable the full benefits of mixed-reactant systems.

4. Development of CMR systems

Generics has begun initial experimental and theoretical investigations of CMR technology. The approach we are following is first to demonstrate proof of principle in single-cells and small stacks, secondly to develop a valid theoretical understanding of how CMR fuel cells work and thirdly to demonstrate significant performance in pre-prototype devices. This approach, we believe, will enable us to work toward demonstrating the applicability and value of the CMR approach to all the main types of fuel cell (PEM, AFC, PAFC, MCFC and SOFC).

The proof of principle of mixed-reactant fuel cells is already well established by the 50-year history of such systems. Our focus has been to demonstrate that the CMR approach—in which a hydrodynamic flow of mixed reactants moves through a porous cell or stack—also works in principle. At Generics we have used a dissolved-reactant alkaline system as the basis of our initial proof of principle experiments. A series of half-cell, single-cell and stacked-cell (series and parallel) experiments were carried out using a commercial anode of Pt–carbon–PTFE catalyst on Ni-mesh (EL05&06, Electro-Chem-Technic) and cathode of MnO_2 –PTFE on Ni-Mesh (EL01&02, Electro-Chem-Technic—note: backing layer of PTFE was removed). For flow-through experiments, porosity of the electrodes was increased by perforating them with a square array of pinholes.

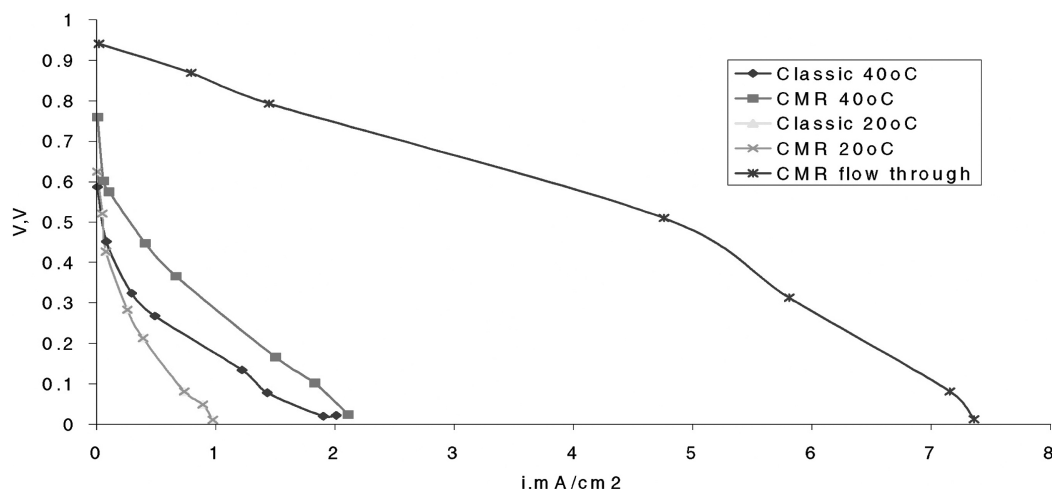


Fig. 1. Performance of flow-through CMR mode (20 °C) compared with mixed-reactant (static CMR) and conventional (classic) modes.

Electrolyte was a 6 M or 10 M solution of potassium hydroxide. Oxidant was air, either dissolved in the electrolyte, dissolved in water, or entrained as bubbles in the electrolyte. Fuel was either methanol dissolved in electrolyte or 0.008 M sodium borohydride (NaBH_4) dissolved in electrolyte.

A three-chamber tubular rig was constructed enabling separate reactant supply to each chamber and also sequential reactant flow through the three chambers. Each chamber was 4 cm in length and were separated by a single anode and single cathode sealed across the diameter of the rig by *o*-rings. External electrical connections were made to the electrodes. In one series of experiments, the performance of an alkaline single-cell in the rig was compared in conventional separated-reactant mode, mixed-reactant mode and in CMR flow-through mode (Fig. 1). In the conventional and mixed-reactant (non-flow-through) modes the electrodes were separated by a 4 cm depth of free 10 M KOH electrolyte, filling the central chamber of the rig.

In the conventional mode, a 0.008 M (3 g l^{-1}) solution of NaBH_4 in 10 M potassium hydroxide (KOH), de-aerated with bubbled nitrogen, was fed to the anode chamber while 10 M KOH saturated with dissolved air was fed to the cathode. In non-flow-through mixed-reactant mode the NaBH_4 –KOH solution was first saturated with bubbled air and then supplied separately to both anode and cathode chambers. In the CMR flow-through mode the same reaction mixture was supplied to the anode chamber, where it flowed through a perforated anode, through the central chamber and then through a perforated cathode before exiting the cathode chamber. In each mode, fluids entirely flooded the three chambers and were pumped through the electrode chambers at a constant rate of 2.5 ml min^{-1} .

Current–voltage data from the three experiments are shown in Fig. 1. At 20 °C, the conventional (“classic” in Fig. 1) mode of fuel cell operation gave identical results to that of the non-flow-through mixed-reactant mode (“CMR”

in Fig. 1). At 40 °C, OCVs and current densities were higher in both cases, with the performance in mixed-reactant mode exceeding that in conventional mode. CMR flow-through mode (which was measured only at 20 °C) gave significantly higher performance than either the conventional or mixed-reactant modes. These results suggest, firstly, that the electrodes in this alkaline system are highly selective toward the respective desired half-cell reactions. Secondly, they suggest that the presence of both reactants at one or other of the electrodes operate in some way to reduce electrode overpotential. Speculative mechanisms could include local decomposition of NaBH_4 to H_2 gas at the cathode surface disrupting the local boundary layer and improving oxygen transport to the cathode, or perhaps through local dissolved oxygen reacting at the anode to increase the rate at which adsorbed reaction products are cleared from the platinum catalyst surfaces. Thirdly, and probably the most significant effect, the results demonstrate that mass-transport of reactants to the electrode catalysts in a CMR flow-through regime considerably exceeds that in a conventional or in a mixed-reactant “flow-by” regime. In the latter, diffusion boundary layers may be substantial and a smaller volume or surface area of catalyst may be exposed to reactant. Overall, this comparison between the three modes of operation supports the various earlier studies reported in the literature on mixed-reactant fuel cells and clearly shows a potential advantage in operating a single fuel cell in CMR flow-through mode.

As part of the second stage of our approach to CMR systems development, we have developed two simple computer models of direct-methanol CMR behaviour based on initial assumptions of the main electrochemical mechanisms and flow modes that determine CMR cell polarisation performance. We anticipate that these models will become increasingly robust and more sophisticated as they are developed and refined through a process of experimental testing and verification. The purpose of the models is to

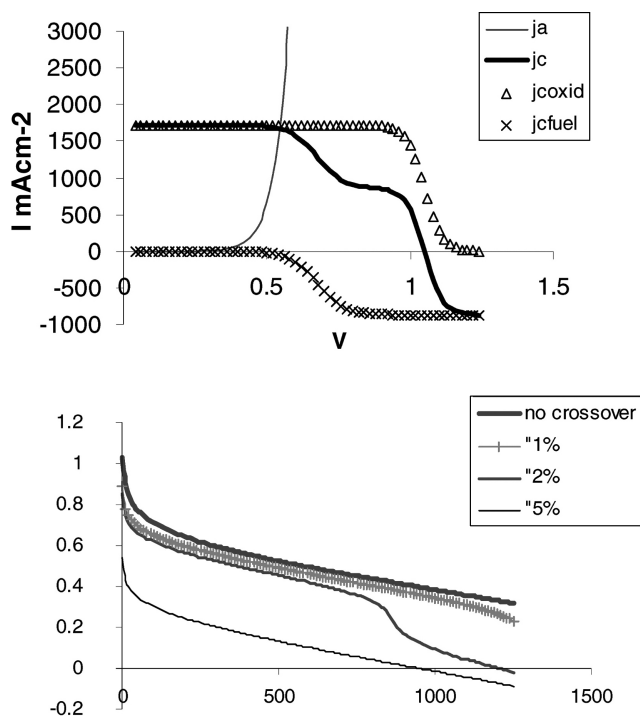


Fig. 2. Simulation of effects on performance of methanol cross-over in a conventional DMFC behaviour using a CMR model. (Upper graph) Simulated half-cell polarisation data for a conventional DMFC with 2% methanol cross-over using a CMR model; (Lower graph) simulated single-cell polarisation data for a conventional DMFC with 0–5% methanol cross-over using a CMR model.

enable the likely performance of future designs of CMR systems to be predicted with reasonable confidence, for example, to help define measurable characteristics required for suitable active materials and to optimise specific microstructures.

The first of our mathematical models of CMR is based on the Butler–Volmer equation that describes electrode potentials and current density in terms of exchange current density and charge transfer coefficients for the various reactions occurring at each electrode. We initially tested the model by using it to predict the expected performance of a “conventional” DMFC with differing extents of fuel cross-over, populating the model with data extracted from Tafel measurements in the literature [34]. The upper graph in Fig. 2 shows predicted anode (j_a) and cathode (j_c) polarisation curves for a DMFC with 2% methanol cross-over, where j_c is the summed result of the competing oxygen reduction (j_{coxid}) and methanol oxidation (j_{cfuel}) reactions occurring at the cathode. The lower graph in Fig. 2 shows predicted cell polarisation curves for a range of methanol cross-over, where each cell curve is calculated from the potential difference of curves $j_c - j_a$ at fixed current. This first electrochemical model assumes that the same reactant mixture is supplied to both electrodes and treats the limits to mass-transport of the reactants simply as a pre-defined maximum flux of each reactant to both electrodes. It does not distinguish, therefore, between the flow-through or flow-across

regimes and does not take into account diffusional boundary layers at the electrodes. Despite this gross simplification, with an assumed fully methanol-selective anode and a completely non-selective cathode, the simulated polarisation curves are comparable to those reported experimentally for the “conventional” DMFC.

In the second of our modeling approaches, we have used a commercial finite element package, Femlab (Comsol AB, Stockholm), to begin to compare the effects of mixed-reactants in different flow regimes on cell polarisation. The single-cell is a direct-methanol PEM MEA consisting of a GDL–Pt–Nafion–Pt/Ru–GDL sandwich (120 μm GDL, 10 μm catalyst, 20 μm electrolyte), where the GDL surfaces are 50% blocked on each side by an interdigitated flow-field current collector. The reactant mixture is a hypothetical single phase 50:50 (v/v) mixture of 1 M methanol and air. The model assumes that in all cases only fuel reacts at the anode and oxygen at the cathode. The model also assumes that in a mixed-reactant environment the cell voltage is 150 mV below standard EMF for the DMFC to allow for less than ideal selectivity of the electrocatalysts. The main basis of the flow model is D’Arcy’s law, which describes the rate of flow of a fluid through a porous network in terms of a specific permeability constant for the network and the viscosity of the fluid. Interdigitated reactant supply to each electrode (as opposed to serpentine flow) is used in the conventional separated-reactant (case 1) and mixed-reactant cases (case 2). In the CMR flow-through case (case 3) the cathode catalyst layer is treated as either flooded with liquid (case 3a) or with gaseous air (case 3b)—oxygen in the cathode backing is in gaseous form in both cases. In all cases the reactant flows were driven at a constant pressure differential of 0.5 atm (Fig. 3).

The results show that at a constant supply pressure the different operating modes are likely to result in very different cell performances. The major difference between case 1 and case 2 is accounted for by the much lower flux of dissolved oxygen to the cathode (compared to gaseous oxygen in case 1) and by the 50% dilution of methanol at the anode by inclusion of air in the mixed-reactant feed. The remaining difference is mainly accounted by the polarisation loss assumed for non-ideal selectivity. The major difference between case 2 and case 3a is the larger and more uniform oxygen supply to the active layer (also more fuel reaches the anode). This results in a more uniform current density distribution and thus a lower polarisation of the electrode. In case 3b, where the liquid mixture does not flood the cathode layer (as would be the case in a gas-reactant system), the resistance to diffusion of oxygen across the cathode is much lower (than in case 3a), increasing the flux of reactants and therefore the current density. The decreased mass-transport resistance makes it possible for the current to be distributed more uniformly and also lowers the kinetic polarisation. Differences between case 3 and case 1 are primarily due to the differences in resistance to reactant flow and to the assumed polarisation loss. In the model, the

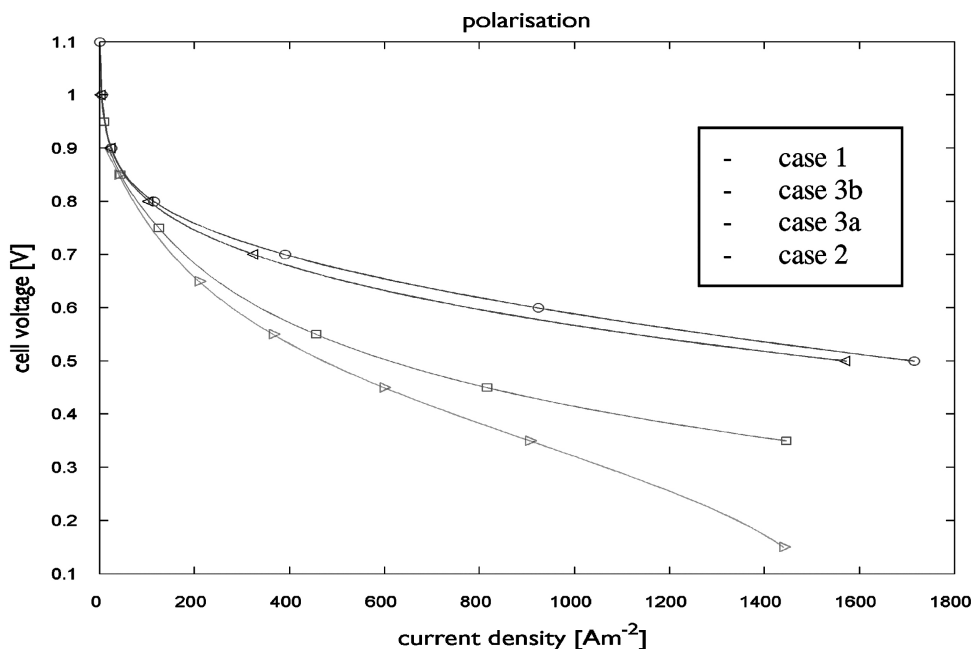


Fig. 3. Predicted polarisation curves for PEM-DMFC operating in conventional mode (case 1), mixed-reactant (non-flow-through CMR) mode (case 2) and CMR flow-through mode (case 3).

permeability of the electrolyte membrane is assumed to be 10% of that of the GDL material. It should therefore be possible to significantly improve the flux of reactants through the cell in CMR mode (case 3) by thinning the electrolyte layer and also by increasing its permeability. Additionally, for purposes of direct comparison in the model, it is assumed that the MEA in case 3 has two GDLs and current collectors that partially block the GDLs. In what might be an ideal flow-through CMR stack, only one GDL should be required to separate each cell and no other current collector or gas distribution structure is required between each cell. With design improvements, such as these, it should be possible to significantly increase the flux of reactants in a CMR system and thereby increase cell current density well above that modeled in case 3b. Furthermore, in this model an interdigitated forced-flow is applied in case 1 rather than the more conventional diffusional serpentine reactant flow adopted in most current fuel cell designs. This suggests that if the mass transfer resistance of a diffusion boundary layer were included in case 1, an even larger advantage could be identified for the CMR mode.

5. Safety of mixed-reactant and CMR systems

Mixing a fuel and oxidant within a fuel cell raises immediate concerns of potential explosion. In reality, a fuel cell stack is largely filled with electrolyte, electrode and separator materials, which will act as a heat sink, eliminating the possibility of explosion. Analogous systems, such as metal-foams or gauzes are well known as means to prevent explosion in storage or usage of explosive mixtures. The

remote possibility of sustained combustion within a mixed-reactant fuel cell will be limited to any open gas supply channels with the structure.

Evidence of the mixed-reactant fuel cells—even high-temperature SOFCs—built and tested in the last 50 years supports the view of safety in these systems. It is, of course, possible to operate with gaseous fuel:oxidant ratios below the explosive limit of the reactants, as several researchers have done. It is also possible to operate with reactant mixtures diluted in an inert carrier, such as nitrogen or water. In liquid mixed-reactant systems, the heat capacity of the liquid medium provides additional protection against any possibility of explosion.

In a CMR fuel cell, where flow of reactants occurs through a porous stacked structure, the elimination of open gas flow channels eliminates any possibility of either sustained combustion or explosion, whatever the mixed-reactant composition. Safety will need to be proved ultimately, of course, by impact, explosion and combustion tests of actual CMR devices.

6. Conclusion

For developers of all of today's fuel cell systems, CMR technology offers immediate benefits in cost, size, power density and reliability at the likely expense of some loss in efficiency. For direct-methanol fuel cells, CMR offers the prospect of an increase in fuel efficiency, as well as these advantages. In the future, with the development of more selective electrocatalysts, the overwhelming advantages of operation in the CMR mode suggest it could displace today's

conventional separate-reactant fuel cell in many application areas.

Acknowledgements

Thanks are due to Prof. Keith Scott of Newcastle University and Dr. Ed Fontes of Comsol AB, for their assistance in the development of fuel cell models.

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