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2011

Shaegh, S. A. M., Nguyen, N. T. & Chan, S. H. (2011). A Review on Membraneless Laminar Flow-Based Fuel Cells. *International Journal of Hydrogen Energy*, 36(9), 5675–5694.

<https://hdl.handle.net/10356/79644>

<https://doi.org/10.1016/j.ijhydene.2011.01.063>

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A Review on Membraneless Laminar Flow-based Fuel Cells

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Abstract

The review article provides a methodical approach for understanding membraneless laminar flow-based fuel cells (LFFCs), also known as microfluidic fuel cells. Membraneless LFFCs benefit from the lamination of multiple streams in a microchannel. The lack of convective mixing leads to a well-defined liquid-liquid interface. Usually, anode and cathode are positioned at both sides of the interface. The liquid-liquid interface is considered as a virtual membrane and ions can travel across the channel to reach the other side and complete the ionic conduction. The advantage of membraneless LFFC is the lack of a physical membrane and the related issues of membrane conditioning can be eliminated or becomes less important. Based on the electrode architectures, membraneless LFFCs in the literature can be categorized into three main types: flow-over design with planar electrodes, flow-through design with three-dimensional porous electrodes, and membraneless LFFCs with air-breathing cathode. Since this paper focuses on reviewing the design considerations of membraneless LFFCs, a concept map is provided for understanding the cross-related problems. The impacts of flow and electrode architecture on cell performance and fuel utilization are discussed. In addition, the main challenges and key issues for further development of membraneless LFFCs are discussed.

Keywords: Microfluidic, Fuel cell, Laminar flow, Membraneless, Review

1. Introduction

Advancement in miniaturization technology led to the emergence of a new class of power generating devices for low-power applications [1]. Small-scale energy conversion schemes are referred to micro power generation for portable and stationary micro devices [2]. Generally, micro power generation can be categorized as (i) chemical-based conversion including micro internal combustion engines and micro turbines [2]; (ii) electrochemical-based conversion such as batteries and fuel cells [3]; and (iii) solid-state direct energy conversion like thermoelectric and photovoltaic microstructures [2].

Among the above energy conversion methods, electrochemical power generators are more competitive for various low-power applications such as cell phones, laptops and PDAs. They do not have moving parts and can be fabricated by relatively simple fabrication processes as compared to heat engines [4]. In contrast to heat engines, electrochemical-based power sources do not normally operate at elevated temperature which is a key design feature for portable devices. The major available power sources for portable electronics and off-the grid applications are batteries [3]. But, demands for longer operational time without frequent recharging has pushed numerous investigations to enhance the capacity of battery, e.g. its energy density, or to deploy alternative power sources such as fuel cells [3].

Microfabrication techniques are usually employed to develop miniature fuel cells [5, 6]. Miniature fuel cells which are also well known as micro fuel cells mainly use the proton exchange membrane. Micro fuel cells are possible power sources for applications ranging from portable electronics to MEMS devices [5].

Since fuel cells utilize fuels with high energy density [7], the operation time span can be longer and only depends on the size of the fuel storage. In contrast, the operation time of batteries is determined by the size of the whole battery as the sole energy storage. In addition, decoupling of fuel cell as energy convertor and fuel cartridge may lead to more flexibility in the design of the fuel cell system.

Technology-based prediction reveals that the technical development of batteries cannot keep pace with ever-increasing power demands of portable electronics available in the markets [3] which are equipped with rising embedded capabilities related to broad-band Internet.

To benefit from the advantages of micro fuel cells to be a long lasting power source, key challenges and major issues must be addressed. Micro fuel cells exploit proton exchange membrane running on methanol or hydrogen with close or open (air-breathing) cathode [8,9]. The main issues of current designs are associated with the membrane. Keeping high proton conductivity of the membrane, for example Nafion, for different working operations is challenging. Water management adds complexity to the fuel cell system. In addition, fuel crossover through membrane is another detrimental issue which degrades the cell performance. Also, swelling and shrinkage of the membrane during water uptake and dehydration deforms the membrane resulting in packaging failure. Therefore, micro fuel cell is not just a matter of downsizing the cell dimensions. To address these membrane-related issues, new materials [10] and novel conceptual designs for micro-scale fuel cells have been proposed [11].

In parallel to the MEMS-based approaches for miniaturizing of conventional power sources, micro/nanofluidics can provide new approaches for energy conversion systems [12]. New functionalities can be explored and created by taking advantage of the specific phenomena which emerge by downsizing the fluidic systems.

The absence of instabilities due to the convective mass transport in laminar flows at low Reynolds numbers allows streams containing different substances with different concentrations to flow side by side through a microchannel. Depending on the Péclet number, an indicator for the relative importance of convection to diffusion, streams can travel down the channel separately. Diffusive mixing of two streams across the liquid-liquid interface results in a concentration gradient. By exploiting the property of such controlled microfluidic interface, different applications and investigations like extraction and separation of molecules [13-15] microfabrication and patterning at the

interface of the streams in a microchannel [16], and micro optofluidic lenses have been achieved [17].

Ferrigno et al. [11] proposed the concept of membraneless fuel cell based on the lamination of two streams in a micro-channel. As shown in Fig. 1, the two streams of oxidant and fuel are introduced into a microchannel with integrated electrodes as the active area for electrochemical reactions. Both anolyte and catholyte have supporting liquid electrolyte to facilitate the ion conduction across the channel. The oxidized fuel or reduced oxidant ions travel across the channel by migration, while the electrons reach the cathode side through an external circuit, Fig. 1(a).

Since fuel and oxidant streams flow down the channel in a parallel manner, the necessity for the presence of a membrane as a separator of two streams is eliminated [11]. Inter-diffusive zone between two streams is restricted to an interfacial width at the center of the channel. To avoid the effects of fuel and oxidant crossover, the electrode-to-electrode spacing should be optimized with design considerations such that Ohmic losses across the channel and pumping energy through the channel are minimum.

A detailed comparison of different membraneless LFFCs in terms of design, fabrication and performance was provided by Kjeang et al. [18]. In the current review, the design considerations for membraneless LFFCs and the effect of electrode structure and their arrangements on cell performance, fuel crossover, and fuel utilization will be discussed. In addition, the major limiting factors of membraneless LFFCs performance are explored, and the possible solutions for further developments are discussed. Also, the various types of fuels, oxidants and electrolytes are reviewed with their corresponding advantages and drawbacks. It is worthy to note that microfluidic biofuel cells can take advantage of the membraneless LFFCs architecture [19, 20]. Microfluidic biofuel cells are out of the scope of this paper, but can benefit from the technology developments of membraneless LFFCs discussed here.

In this paper a concept map is used to give a general overview about the effective parameters and mechanisms on the performance of a membraneless LFFC, Fig. 2. This concept map can be used for

the cross-related problems to provide a clear overview for reading and understanding the text [21].

2. Fundamentals

Membraneless LFFCs follows the basic electrochemical principles of membrane-based fuel cells. The only main difference is that the role of membrane as a charge transport media and as a separator of electrodes is represented by creating a confined liquid-liquid interface in a microchannel. Usually, microchannels are defined as channels with characteristic dimension less than 1 mm and greater than 1 μm [22], and the fluid manipulation inside the microchannels is known as microfluidics.

With a scale factor of R , the ratio of surface to volume is $\left(\frac{R^2}{R^3} = R^{-1}\right)$ which decreases with miniaturization. Microfluidic systems can harness the scale-dependence of interface properties, to exploit a broad series of applications [23]. As fluidic systems are reduced in size, laminar flow regime at low Reynolds numbers is established. In this case, surface-based effects including surface tension or viscosity can dominate over volume-based effects, offering new micro-scale phenomena, for instance confined liquid-liquid interface in a microchannel with co-laminar streams can be achieved.

Due to the continuum and laminar nature of liquids at microchannels [22], mass conservation for fluid flows obeys the continuity equation:

$$\frac{\partial \rho}{\partial t} + \nabla(\rho \vec{u}) = 0 \quad (1)$$

A constant fluid density (ρ) leads to the incompressible flow condition, $\nabla \vec{u} = 0$. The Navier-Stokes equations can be solved to determine velocity field ($\vec{u}$):

$$\rho \left(\frac{\partial \vec{u}}{\partial t} + \vec{u} \nabla \vec{u} \right) = -\nabla p + \mu \nabla^2 \vec{u} + \vec{f} \quad (2)$$

where p is the pressure and $\vec{f}$ includes all body forces per unit volume.

As shown in Fig. 1(a), two separate streams of fuel and oxidant are introduced into the channel,

which come in contact to create a parallel co-laminar flow in the channel with a liquid-liquid interface. This interface takes action as a separator of fuel and oxidant streams. Current collectors and electrodes with appropriate catalyst layer on the surface are fabricated on channel walls where the electrochemical reactions take place. To obtain charge transport between two electrodes, both fuel and oxidant solutions should contain ionic conductivity which is obtained by adding supportive electrolyte to both streams. The supporting electrolyte contains hydroxide or hydronium ions like diluted solutions of potassium hydroxide or sulfuric acid.

For a fuel-oxidant configuration as shown in equation (3) at given temperature and pressure, the theoretical equilibrium open-circuit potential of a given oxidation-reduction reaction within the cell is determined by the Nernst equation:

$$E^0(T, P) = E^0 + \frac{R_u T}{nF} \ln \left[\left(\frac{a_A^{v_A} a_B^{v_B}}{a_C^{v_C} a_D^{v_D}} \right) \right] \quad (3)$$

where E^0 is the equilibrium potential at standard state and a is the activity of each species. For aqueous species, the activity is estimated by the concentration. Since there is no membrane between the fuel and oxidant streams, pH of the two streams can be modified individually to increase the half-cell potentials. The theoretical cell potential is degraded by the anodic and cathodic activation losses ($\eta_{a,a}, \eta_{a,c}$), ohmic losses (η_r), anodic and cathodic mass-transport losses ($\eta_{m,a}, \eta_{m,c}$), and other losses (η_x):

$$E_{\text{cell}} = E^0(T, P) - \eta_{a,a} - |\eta_{a,c}| - \eta_r - \eta_{m,a} - |\eta_{m,c}| - \eta_x \quad (4)$$

Here, η_x represents the crossover effect of fuel/oxidizer through the electrolyte to the opposite electrode or internal short circuits in the cell which is responsible for more departure of open-circuit potential from Nernst equilibrium voltage.

Due to the slow electro oxidation reaction of aqueous liquids such as formic acid and methanol, the activation losses are generally higher than a hydrogen-fed PEM fuel cell, and the cell potential drops

rapidly.

Ohmic losses are mainly attributed to the electrolyte ionic resistivity ($R_{electrolyte}$) and the external resistance of electrodes and connections ($R_{external}$) where the current (i) is drawn from the cell:

$$\eta_r = i(R_{electrolyte} + R_{external}) \quad (5)$$

Ohmic resistance of the supporting electrolyte for charge transport between electrodes depends on anode-to-cathode spacing or the charge-transport length (d), cross-sectional area of charge transport (A) and the ionic conductivity (σ):

$$R_{electrical} = \frac{d}{\sigma A} \quad (6)$$

Typical bulk through-plane conductivity of Nafion[®] as proton exchange membrane is around 0.1 S/cm² at 100% relative humidity (RH) and room temperature [24] with a typical membrane thickness of 50-200 μ m. In contrast, the conductivity of 0.5M sulfuric acid as a common supporting electrolyte is on the order of 0.2 S/cm². Anode to cathode spacing in a membraneless LFFC is generally at the range of 0.5 mm-1.5 mm, which results in higher total ohmic losses than that of PEM fuel cells. Low concentration of oxidant or fuel is the main source of mass transfer losses. Mass transfer losses play a significant role on degradation of cell potential at high current densities while a cell is operating at low flow rates due to slow replenishment of depletion layer over the electrodes. The following sections of the paper provide detailed discussions about these four losses with the available or potential solutions.

While the electrochemical reactions occur, fuel and oxidant are consumed over the corresponding electrodes to generate the current. Current density distribution is estimated by Butler-Volmer equation as a function of volumetric exchange current of a given electrode (i_o) at reference concentration ($C_{i,ref}$):

$$J_o = i_o \left(\frac{C_i}{C_{i,ref}} \right)^{\beta_i} \left[\exp\left(\frac{\alpha_a F \eta}{R_u T} \right) - \exp\left(- \frac{\alpha_c F \eta}{RT} \right) \right] \quad (7)$$

Here, C_i is concentration of the species “ i ” which refers to fuel or oxidant, and β_i is the reaction order of the species for the elementary charge transfer step. α_a and α_c are the anodic and cathodic charge transfer coefficients, R is the universal gas constant and T is the operating temperature, F is the Faraday’s constant and η is the surface overpotential:

$$\eta = \phi_s - \phi_e - E^0(T, P) \quad (8)$$

where ϕ_s and ϕ_e are the potential of electrode and electrolyte. The species concentration distribution over the electrodes is governed by diffusion-convection transport, and can be calculated by solving mass conservation equation:

$$\nabla(-D_i \nabla C_i + C_i \vec{u}) = S_i \quad (9)$$

where D_i is the diffusion coefficient of species “ i ” and S_i is the net rate of change of species “ i ” by electrochemical reactions over anode and cathode, and represents the rate of consumed species per cubic meter:

$$S_i = \frac{J_o}{nF} \quad (10)$$

Increase in the flow rate of fuel and oxidant accelerate the replenishment of the depletion zone over the electrodes and develop the maximum cell current and power density at the expense of low fuel utilization:

$$\varepsilon_{fuel} = \frac{J}{nFv_{fuel}} \quad (11)$$

where, J is the generated cell current and U_{fuel} represents the rate at which fuel is supplied to the fuel cell with the unit of mol/sec. Low fuel utilization dictates the implementation a recycling system for fuel and oxidant which is not practical.

3. Designs and flow architectures of membraneless LFFCs

The interface between two streams with supporting electrolytes represents a virtual membrane by providing (i) an ion conductive media with (ii) effective controlled mixing of reactants across the cell.

In brief, membraneless LFFCs can benefit from the following advantages of microfluidics:

- a. Membrane is eliminated thus reducing the size of the cell and enhancing the flexibility in cell design and fabrication including miniaturization [11, 25].
- b. Since both streams flow through a single channel, some design considerations for fuel and oxidant delivery systems are eliminated simplifying sealing and packaging requirements. Furthermore, the composition of fuel and oxidant streams can be tailored individually to maximize reaction kinetics at anode and cathode [26].
- c. Membrane-related issues such as water management, membrane fouling and damaging partially disappear [11, 27].
- d. Membraneless LFFC as a power source is compatible with other microfluidic systems such as Lab on Chip devices.

Low fuel utilization per single pass and low power output are considered as the most major drawbacks of membraneless LFFCs. Since both electrodes and streams are usually placed in a single channel, the flow architecture of streams has significant effects on the performance of membraneless LFFC. In the past, numerous investigations were carried out to study the effect of flow architecture, and electrode structures/ arrangements on cell performance.

Depending on the design of the implemented electrodes, membraneless LFFC are categorized into (i) flow-over type with planar electrodes, (ii) flow-through type with three-dimensional porous electrodes, and (iii) membraneless LFFC with air-breathing cathode. All designs exploit common fuels and oxidants and can be fabricated by conventional fabrication methods with the same level of precision. All designs can use either alkaline or acidic electrolytes.

Different materials and processing considerations must be taken into account to fabricate a reliable fuel cell. The design considerations are [28]:

- a. Carrier substrate to form the channel and the desired geometry.
- b. Structure of the catalyst and its deposition method on the supporting substrate of catalyst.
- c. Assembly method of the electrodes and channel structures to provide a liquid-tight sealed cell with interfaces to instrumentation and fuel/oxidant delivery systems.

3.1. Flow-over type

3.1.1. Electrode location

Two electrodes of a membraneless LFFC are usually integrated in a micro channel, Fig. 1(a). The fuel and oxidant streams in the channel come into contact in two configurations: side-by-side streaming with vertical fuel-oxidant interface and vertically-layered streaming with horizontal fuel-oxidant interface. For both streaming configurations, two electrodes can be positioned in top-bottom configuration [Fig. 1(b)], side walls [Fig. 1(c)], or both electrodes on bottom wall [Fig. 1(d)]. In addition, the electrodes can be positioned in a grooved channel [Fig. 1(e)] to control bubble generation, or an array of electrodes can be implemented in a channel [Fig. 1(f)].

For the vertical interface of co-laminar streams, the gravity-induced reorientation of the interface may occur provided that fuel and oxidant streams have very different densities. Hence, as both streams flow down the channel, the denser fluid is forced by the gravity-induced pressure mismatch at the interface to occupy the lower portion of the microchannel gradually [29]. Due to this reorientation, the operation of membraneless LFFC begins to fail since fuel oxidation and oxidant reduction are no longer restricted to the appropriate electrodes. For horizontal liquid-liquid interface, the mismatch of densities may speed up the broadening of inter-diffusive zone if the denser fluid is on the top layer.

As shown in Fig. 1, flow-over designs generally provide streaming of fuel and oxidant over planar electrodes. Only a fraction of fuel and oxidant streams in adjacent to the catalyst layer participate in electrocatalytic reactions. Due to the lack of effective convective mass transport, a depletion

boundary layer with low concentration of reactant grows over both electrodes. To enhance fuel utilization in flow-over designs, an improved design of electrodes was implemented in the channel to provide more active area for electrochemical reactions, as shown in Fig. 1(f). The graphite rods at the center of the channel, are electrically insulated [27].

3.1.2. Carrier substrate

Microchannels are typically fabricated by rapid prototyping techniques, using standard photolithography, soft lithography or laser micro-machining. In some designs of membraneless LFFCs with side-by-side streaming, the channel structures are fabricated using polydimethylsiloxane (PDMS) molding and then sealed to a solid substrate with electrodes [30,31]. For sealing the channel, glass or PDMS can be used with plasma-treatment. In addition, the channels can become hydrophilic by exposure to oxygen plasma to enhance wetting properties. Several characteristics making PDMS useful for microfluidic devices are easy fabrication (rapid prototyping, sealing, interfacing), transparency in the UV—visible regions, chemical inertness, low polarity, low electrical conductivity, elasticity and low cost fabrication [32]. PDMS does not swell in contact with water and acids [32]

Due to the relatively high solubility and permeability of hydrogen and oxygen in PDMS ($D_{H_2} = 1.4 \times 10^{-4} \text{ cm}^2/\text{s}$ and $D_{O_2} = 34 \times 10^{-5} \text{ cm}^2/\text{s}$ at 35 °C) [33], gas reactants can be supplied through thin layers of PDMS to a pair of electrodes separated by a channel containing sulfuric acid or sodium hydroxide as electrolyte [34,35]. Using this concept, the achieved power densities of the cells running on dissolved hydrogen/oxygen [35] and hydrogen/air [34] were around $0.7 \text{ mW}/\text{cm}^2$ as restricted by permeation rate of dissolved hydrogen through PDMS.

Choban et al. [26] used graphite as substrate to serve three functions: current collector, catalyst support structure, and edificial element. As shown in Fig. 3(a), the graphite plates are placed side-by-side with a specific spacing to form the width of the channel. Before assembling, the catalyst

is applied to the graphite plates. To seal the channel, 1-mm thick poly-carbonate slabs with thin films of PDMS were used as gasket.

Polymethylmethacrylate (PMMA) is another polymeric material frequently employed for microfluidics and micro fuel cells [8]. PMMA is one of the thermoplastic polymers, which are usually linearly-linked and can be softened by applying heat at above the glass transition temperature [36]. PMMA has a non-crystalline structure with 92% light transmittance in the visible spectrum. This material also has other excellent properties such as low frictional coefficient, high chemical resistance and good electrical insulation. All the above features and properties make PMMA a good substrate for microfluidic devices, especially for those involve chemical reactions [36].

A PMMA substrate can be micro-machined in many ways, such as X-ray exposure and subsequent developing, hot embossing and laser machining [36]. For laser machining, the cross section of the microchannel depends on the shape of the laser beam, its moving speed, the laser power and the thermal diffusivity of substrate material. The energy of the laser beam has a Gaussian distribution, thus the cross section of the channel also has a Gaussian shape [36].

Li et al. [37] used infrared CO₂ laser to engrave channels in PMMA structure to fabricate a membraneless fuel cell. In this design, three PMMA sheets were used to create the channel, Fig. 3(b). A slit is produced in the 1-mm middle sheet using laser and is sandwiched between the top and bottom PMMA stencils using an adhesive layer. The bottom layer works as the electrode support and liquid sealing plate. A 100 nm gold layer was sputtered on the surface of the PMMA sheet to reduce the contact resistance. This gold layer acts as the current collector. The surfaces of the PMMA sheets were mechanically treated with fine sandpaper (1200 grit) to improve the surface roughness and to improve the adhesion of the gold layer to the substrate. Outlet and inlet holes were machined at the top PMMA piece. Pt-Ru and Pt catalyst inks with a loading of 4.5 mg/cm² were wet-sprayed on the gold layer to make anode and cathode, respectively.

Rigid microchannels are also fabricated in silicon using photolithography processes [28,38]. Since silicon is stable against thermal deformation, silicon channels and substrates can be used to investigate temperature dependent fuel cell performance while, platinum can be deposited on a metallic adhesion layer using E-beam evaporation technique to present electrodes [28]. By exploiting the standard photolithography for silicon processing, the design can benefit from the ease of fabrication where parameters can be varied. Therefore optimization of microchannel dimension can be carried out in a relatively short time period [28], Fig. 3(c).

3.1.3. Fuel and oxidant delivery system

Fuel and oxidant concentrations decrease because of the ongoing electro oxidation of fuel and electro reduction of oxidant over anode and cathode. Due to the lack of convective mass transport to replenish fresh reactants to the catalytic active area, a depletion boundary layer over the catalyst-covered electrodes is formed [39] as shown in Fig. 4.

Equation (7) indicates that current density (J_o) is a function of reactant concentration (C_i). If effective replenishment of the depletion layer does not exist, the reactant concentration over the active area of electrodes drops dramatically. In this case, only the first few millimeters of the electrode contribute the most to current collection [40] limiting the electrode length. In addition, to control diffusive mixing and consequent parasitic losses, the length of the channel must be restricted [41].

To overcome the limitation of mass transport to active sites, Yoon et al. [42] introduce three methods to enhance the performance of membraneless LFFC by controlling the depletion boundary layer, Fig. 5. Mass transport to the planar active areas on the channel walls can be enhanced by (i) using “multiples inlets” to add fresh reactants to the microchannel and to replenish the depletion zones; (ii) removing the depleted zone through multiple outlets, and (iii) implementing herringbone ridges to support the depleted layers with fresh reactant from the

middle of the microchannel created by advection. Adding ridges to one wall increases 10-40% current density.

Approaches (i) and (ii) are most appropriate to enhance the reactant conversion rate because they remove or replenish depletion zones providing a continuous high concentration of reactants near the active area. These approaches are suitable for enhancing the power density. Approach (iii) is suitable for enhancing fuel utilization in a single pass improving the reactant conversion efficiency. However, in terms of packaging and fabrication, approaches (i) and (ii) benefit from a single-height design, but require more space for assembly of multiple inlets/outlets. It is noteworthy that the pumping energy for approaches (i) and (ii) is larger than approach (iii).

The idea of passive control of depletion layer to develop the maximum current density without using additional power triggered investigations on the effect of multiple consecutive electrodes on the current density and fuel utilization [19, 43]. Lim et al. [19] proposed that each electrode can be made of an array of microelectrodes. Splitting the length of an electrode into two or more sections to make shorter electrodes with spacing equal to three times their length can avoid the continuous increase in thickness of the depleted layer. Thus, a 25% increase in maximum power density in comparison with a single electrode device with identical active area was achieved. Lee et al. [43] optimized the electrode length and gap between the consecutive electrodes using numerical simulations for a membraneless LFFC running on 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid) (ABTS) and oxidized ABTS. For a membraneless LFFC with a gap between the two electrodes, the efficiency of the second electrode is developed as the gap between the subsequent electrodes is longer. It was suggested that incorporating the very small electrodes within the membraneless LFFC should maximize the current density while decreasing the amount of unspent fuel.

3.2.Flow-through design

In a flow-through design, the reactant streams pass through a three-dimensional porous electrode

including the catalytic active area. As depicted in Fig. 6(a), the whole streams pass through the 3D electrode. In some designs the fuel and oxidant streams are divided into many sub-streams providing a so-called “multiple inlets” approach to refresh the depletion boundary layer, Fig. 6(b). Due to the effective diffusive/ convective mass transport through 3D electrodes, the depletion boundary layer is replenished continuously resulting in a higher rate of fuel utilization and greater power output. Flow-through design can provide an approximately constant concentration of reactant over active site for electrocatalysis.

Salloum et al. [44] proposed a convective flow membrane-less LFFC with porous disk electrodes, Fig. 6(a). The carrier substrate was fabricated using PMMA. Formic acid in sulfuric acid as fuel stream was introduced through an inlet from the center of the disk and undergoes oxidation through the carbon paper covered by catalyst nanoparticles as its porous anode. The oxidant stream, potassium permanganate in sulfuric acid, was introduced concentrically through a ring of inlets. The oxidant was reduced and then mixed with the oxidized fuel and a 2-mm gap between anode and cathode preventing short circuit due to the backflow of the oxidant.

Ion transport was developed due to convective transport. Fuel utilization was improved up to 58% and independent control of fuel and oxidant flow rate were achieved. Experimental results indicated that by increasing the fuel flow rates, fuel utilization is decreased from 58% at 100 $\mu\text{l}/\text{min}$ to 4% at 5 ml/min . Increasing the concentration of sulfuric acid as supporting electrolyte increases the maximum power density from $\sim 1.5 \text{ mW}/\text{cm}^2$ to $\sim 3 \text{ mW}/\text{cm}^2$ due to the decreasing Ohmic losses.

The concept of so-called “multiple inlets” was introduced by Sinton’s group [45]. A flow-through design was proposed without imposing fluidic networks of inlets for adding fresh reactants. The whole cell was fabricated in PDMS. As shown in Fig. 6(b), hydrophilic porous fiber-based carbon paper, with the main application for making gas diffusion layer in proton exchange membrane fuel cell (PEMFC), was cut in strip shape and placed in two compartments.

High porosity of carbon paper, ~87% (HGP-H 90 from Toray), provides large surface area for electrochemical reactions and enhances the fuel utilization due to the improved diffusive/convective mass transport [45]. Running the cell on all-vanadium redox species, peak power density of 131 mW/cm² was obtained at a flow rate of 300 µl/min.

3.3. Air-breathing designs

Mass transfer and diffusivity of dissolved oxygen as an oxidant in aqueous media (2×10^{-5} cm²/s) limits the performance of membraneless LFFCs running on dissolved oxygen. In addition, low concentration of dissolved oxygen in aqueous media (2-4 mM) cannot sufficiently provide for the replenishment of depletion boundary layer over the cathode. Exploiting a gas diffusion electrode (GDE) on a side wall of the channel facilitates the cell to access the high concentration of oxygen in air of 10 mM and the diffusivity of 0.2 cm²/s four order of magnitude higher than that in aqueous media.

The proof of concept for a membraneless LFFC with air-breathing cathode was proposed by Kenis' research group in 2005 [46]. As shown in Fig. 7(a) and (b), gas diffusion electrode (GDE), made of Toray carbon paper covered by catalyst ink containing platinum black nanoparticles, was implemented at the top wall as air-breathing cathode. The channel was made in PMMA which is bonded to a graphite plate covered with palladium black nanoparticles as a flow-over anode.

Since the oxidant stream is eliminated in this design, a stream of electrolyte is needed to separate the fuel stream from direct exposure to the cathode avoiding fuel crossover losses and catalyst poisoning. Formic acid with a concentration of 1 M was used as fuel, while 0.5 M sulfuric acid in both fuel and electrolyte streams allows proton conduction across the channel. In this case, a peak current density of 130 mA/cm² and a power density of 26 mW/cm² were achieved. Anode and cathode potentials obtained using Ag/AgCl reference electrode revealed that oxygen concentration is not the source of limiting performance for an air-breathing membraneless LFFC

[47].

Tominaka et al. [25] reported a monolithic design for an air-breathing membraneless LFFC running on methanol. The whole cell, which was a reservoir with open top, was fabricated in silicon as a monolithic structure that does not need the electrolyte stream to separate fuel stream from the cathode. Palladium-cobalt (Pd-Co) alloy was electrodeposited on a thin layer of gold and worked as the current collector. In this design with full passive fuel and oxidant delivery systems, oxygen was taken through a porous cathode. A 2 M methanol solution containing a sulfuric acid as supporting electrolyte is dropped onto the end of the micro channel. Open-circuit voltage and net maximum power of this fuel cell reached 0.5 V and 1.4 μ W, respectively.

3.4. Performance comparison

To provide a quantitative performance comparison, performance of different membraneless LFFCs based on the electrode design is reviewed in Table 1 and Fig. 8. Since cell kinetics depend on the fuel type, only membraneless LFFCs running on formic acid or methanol are discussed. Table 2 provides some design features to obtain the maximum power density of three different flow architectures running on formic acid or methanol.

Table 1 shows that the order of magnitude for the power density of membraneless LFFCs of flow-over design ranges from 0.1 mW/cm² to 1 mW/cm², and for the flow-through design from 1 to 10 mW/cm². The low performance of flow-over designs is mainly attributed to low oxidant concentration at catholyte and the growth of depletion layer over electrodes. The performance for flow-through design is associated with the enhancement of catalytic reaction through porous and 3D electrodes with effective replenishment of reactant over active sites. The main reason for higher performance of air-breathing membraneless LFFCs is the higher rate of oxygen transport to the cathode from ambient air. Since oxygen is provided from air through GDE, the oxygen concentration over the active site of the cathode is almost constant, thus enhancing the current

generation.

4. Performance limiting factors

To identify the performance limiting factors of membraneless LFFCs, experimental and theoretical approaches including using reference electrode [47,48] and numerical simulation of the coupled transport phenomena and electrochemical reactions have been reported [39,40,43,54-59]. The main objective of using reference electrode is to measure the voltage losses due to different limiting parameters of an electrochemical system such as kinetics, mass transfer and Ohmic resistance of individual electrodes [60]. The obtained results from the reference electrodes can be used to identify the problems in the cell and to develop solutions [60].

Choban et al. [48] utilized external reference electrodes to identify the limiting factors in a membraneless LFFC. The overall cell performance, current-voltage experiment, indicates the mass transport limitation at high current densities, but this experiment does not identify whether this limitation takes place at anode or the cathode. By using the external Ag/AgCl reference electrode, connected to the membraneless LFFC, the individual contribution of each electrode loss to the overall cell performance was provided. The results indicated that the mass transport at the cathode is the limiting factor at high current densities for this specific design due to the low solubility of oxygen in the water-based electrolyte [48].

Jayashree et al. [47] exploited external Ag/AgCl reference electrode to identify the mass transfer-limited electrode in a membraneless LFFC with air-breathing cathode running on 1 M methanol. Supporting electrolytes were 0.5 M H₂SO₄ or 1 M KOH to investigate the effect of acidic or alkaline electrolyte on the whole cell performance. Shape of cathode polarization curve confirmed that the gas diffusion electrode allowed higher rate of oxygen transport to the cathode as compared to a membraneless LFFC running on dissolved oxygen.

4.1. Inter-diffusive mixing zone and fuel crossover

In addition to low oxidant concentration over the catalytic areas and slow mass transfer [49], diffusive mixing at the liquid-liquid interface can be considered as another major issue. The two consequences of diffusive mixing which degrades the overall cell performance and efficiency are: (i) reduction in the concentrations of fuel/oxidant streams leading to decreased current density, and (ii) fuel crossover to cathode side leading to degradation of open-circuit potential. Since platinum is usually used for oxygen reduction at the cathode side, crossover fuel oxidation over Pt can block the catalytic active sites by the adsorbed CO intermediates decreasing the rate of electroreduction of oxygen at the cathode.

In a microchannel, which is sufficiently small to yield a low Reynolds number ($Re < 1$), two separate streams can be brought together enabling the diffusion of particles and ion between two non-mixing streams [13]. The two mechanisms facilitating proton transport from anode to cathode are: (i) diffusive transport due to gradient in proton concentration between anode and cathode and (ii) electromigration due to the voltage gradient between electrodes. By balancing the charge flux generated by a given voltage gradient (j_v) and the highest attainable charge flux (j_c) due to a concentration gradient across an ion conductor, equation (12) can be used to determine the voltage required to produce an equivalent charge flux as follows [61]:

$$V = \frac{RT}{zF} \quad (12)$$

where R and T are the universal gas constant and the temperature, respectively; z is the valence of the species and F is the Faraday's constant.

At room temperature and $z = 1$, a voltage drop of 25.7 mV across the thickness of the ion conductor has the same effect as the maximum chemical driving force provided by the concentration gradient. Since membraneless LFFCs generally work at room temperature, the charge transport across the channel filled by electrolyte is dominated by electrical driving force rather than the chemical potential driving force.

Inter-diffusive width between two streams is highly dependent on the mean residence time of streams in the channel. The mean residence time is fixed by the dimensions of channel width, channel height, channel length and the input flow rate [62]. In co-laminar streams with different viscosities, the velocity profile will adjust, so that more of the channel width is occupied by the more viscous fluid, which also moves with a slower mean velocity [62].

For a given device geometry including liquids of similar density, the mean inter-diffusive distance across the channel width (δ), as shown in Fig. 9(a) and (b), depends on the flow rates, the distance along the channel (x), and the diffusion coefficients of the species of interest. If the resulting mean inter-diffusive distance is significantly less than the channel height (H), molecules near the top and bottom of the device would diffuse more effectively because of the further residence time in these regions of the channel, resulting in the “butterfly effect” [62] (Fig. 9(b)). It is worthy to note that increasing the flow rate can decrease the average residence time and thereby decrease the extent of diffusive mixing of the two streams at a fixed observation point [62]. As Equation (14) indicates, near the top and bottom walls of the channel, diffusive broadening $\delta(x)$ across the fluid—fluid interface scales to one-third power of the axial distance (x) along the channel and scales inversely to one-third power of the maximum flow velocity [63]:

$$\delta_{wall}(x) \propto \left(\frac{DHx}{\bar{u}} \right)^{\frac{1}{3}} \quad (13)$$

where D is the diffusion coefficient, H is the channel height and $\bar{u}$ is the mean velocity through the channel. The extension of diffusive mixing near the middle of the channel, where the flow speed is nearly uniform, scales to one-half power of the axial distance (x) along the channel and inversely to the one-half power of the average flow velocity [63]:

$$\delta_{center}(x) \propto \left(\frac{Dx}{\bar{u}} \right)^{\frac{1}{2}} \quad (14)$$

Decreasing the channel height while keeping other parameters constant decreases Péclet number

$(Pe = \frac{uH}{D})$ and makes the difference between the diffusion near the top and bottom walls and in the center less dramatic. For high Péclet-number flow regimes inter-diffusive broadening decreases near the top and bottom walls [63].

Diffusive broadening is the main cause of reactant crossover. The main effects of fuel crossover are decreasing the fuel concentrations over anode leading to a decrease in open-circuit potential.

In a detailed study, Sprague et al. [64] calculated the parasitic crossover current at both anode and cathode of a membraneless LFFC with planar and top-bottom electrodes arrangements running by both aqueous oxidant and fuel. The model utilizes the Poisson-Nernst-Planck (PNP) equations that provide a more general treatment for studying the reactant crossover than the common methods. Common methods assume that the crossover reactant is fully utilized over the electrode producing crossover current [65]. The new model can capture the concentration change of crossover reactant along the opposite electrode. Using this model it was observed that by decreasing the channel height (electrode-to-electrode spacing) fuel crossover increases and open-circuit potential decreases. For the narrowest channel with a height of 50 μm , calculations were carried out for two cases: (1) without considering the crossover current and (2) with considering the crossover current. At a given operating conditions of the membraneless LFFC, a huge drop in the open-circuit potential from 0.9 V for case (1) to 0.1 V for case (2) occurs. Also, at the narrowest channel with a height of 50 μm , the potential distribution across the channel was significantly affected by the reactant crossover. Such observations suggest a reconsideration of common assumptions used in the modeling and simulation of reactant crossover in fuel cells.

Shaegh et al. [39] observed in an experimental-numerical investigation over a membraneless LFFC with air-breathing fuel cell that by decreasing the flow rate from 500 $\mu\text{l/min}$ to 10 $\mu\text{l/min}$, open-circuit potential (OCP) drops from 0.78 V to 0.58 V. The numerical simulation of the same fabricated cell indicated that at 500 $\mu\text{l/min}$ the formic acid concentration over the cathode is almost zero while for the flow rate of 10 $\mu\text{l/min}$, the average concentration of formic acid is 250

mol/m³ which is an indication of lower OCP due to mixed potential.

4.2. Optimization of channel geometry

Since membraneless LFFCs generally exploit co-laminar flows in a single channel, flow structure has significant effects on the interaction between two streams. Bazylak and co-workers [39] established a 3D CFD model to simulate a membraneless LFFC. In their numerical simulation, coupled electrochemical and mass transport phenomena were solved to simulate the depletion and mixing regions of formic acid and dissolved oxygen. Numerical results showed that both microchannel and electrode geometry play key roles in mass transport and inter-diffusive zone. A rectangular channel with high aspect ratio (length/width) and tapered electrodes was proposed as an optimum design (Fig. 10(a) and (b)). Using the extended electrode designs, fuel utilization was improved by 50% while minimizing fuel/oxidant mixing in membraneless LFFC. It is also noteworthy that the areas of cathodes and anodes and the gap between them must be set very precisely to avoid the overlap of the diffusively mixed region with the electrodes. Numerical analysis revealed that decreasing the inlet velocity from 0.1 to 0.02 m/s increases the fuel utilization from 8% to 23%, while there is only 3% increase in cross-stream mixing at the outlet.

In a numerical optimization of the channel geometry, Ahmed et al. [66] explored the effect of a Ψ -shape geometry on fuel utilization and mixing width. Streams of 0.5 M formic acid in 0.1 M H₂SO₄ and 1.25 mM dissolved O₂ in 0.1 M sulfuric acid were interconnected by a stream of 0.1 M sulfuric acid solution working as proton-conducting fluid. Three streams are introduced into the cell from three separate inlets, Fig. 10(c) and (d). Numerical modeling considering both of electrochemical reaction and flow field effects indicated that by optimizing the channel dimensions and reaction surface areas, fuel utilization can be improved by up to 86%. Because of the restricted mixing of fuel and oxidant through the proton-conducting channel, this flow configuration is suitable for portable applications.

Sun et al. [67] integrated a blank electrolyte stream of 0.5 M H₂SO₄ in a Ψ -shaped microchannel to separate two streams of 2.1 M formic acid and 0.144 M potassium permanganate as shown schematically in Fig. 10(c). Experimental results indicated that optimized flow rate can enhance the open-circuit potential which is an indication for controlling the diffusive crossover of fuel. Using the concept of the blank electrolyte stream, Salloum and Posner [68] proposed a counter-flow membraneless LFFC with 2 M sulfuric acid as separating electrolyte stream to control diffusive mixing of 50 mM vanadium redox species in 1 M sulfuric acid, Fig. 11(a). In this case, a peak power density of 5 mW/cm² was observed at a fuel/oxidant flow rate of 300 μ l/min and electrolyte flow rate of 30 μ l/min.

Another strategy to decrease the fuel crossover is implementing a thin nanoporous separator at the interface of the two streams [52, 69], but in the expense of increased cost for design, fabrication and packaging of this more complex concept. As shown in Fig. 11(b), Hollinger et al. [52] positioned a thin layer of polycarbonate with 0.05 μ m pore size and pore density of 6×10^8 pores cm⁻² at the fuel-electrolyte interface which reduced the liquid-liquid contact between two streams by 98.8% [52]. The separator is not selective to methanol and may also reduce the proton transport across the channel. The diffusion coefficient of protons in an aqueous media ($D_{H^+ (water)} = 9.31 \times 10^{-5}$ cm²/s) is one order of magnitude higher than that of methanol in aqueous media ($D_{MeOH (water)} = 1.58 \times 10^{-5}$ cm²/s). Moreover, the proton diffusion is facilitated by the potential gradient between the electrodes while the only driving force for methanol transport is the concentration gradient across the channel. Hence, the separator has a greater effect on the mitigation of methanol crossover process than the rapid proton transport phenomenon.

The above design improvement can decrease the electrode-to-electrode distance, while the rate of fuel diffusion to the electrolyte can be decreased significantly. The catalyst layer of the cathode was covered by a thin layer of Nafion using a hot press process. Since the diffusion coefficient of methanol in Nafion is one order of magnitude smaller than the diffusion coefficient in water

($D_{\text{MeOH (Nafion)}} = 3.0 \times 10^{-6} \text{ cm}^2/\text{s}$ vs. $D_{\text{MeOH (water)}} = 1.58 \times 10^{-5} \text{ cm}^2/\text{s}$), this layer of Nafion can mitigate the rate of the methanol diffusion to cathode catalyst. Another method to alleviate fuel crossover by reducing the mass transport is using low fuel concentration. In this method, the driving force for fuel diffusion is decreased. The combination of these two methods can provide a platform for operation over a wide range of fuel concentrations. With these designs, the maximum power density was improved by a factor of 2.5. The peak power density of a single cell operating at 80 °C with 1 M of methanol and O₂ supply and without a separator and Nafion on the cathode is 28 mW/cm². Adding either Nafion on the cathode or a separator enhances the maximum power density to more than 40 mW/cm². By exploiting both methods, the peak power density reached 70 mW/cm².

Fuel can diffuse through the fuel–electrolyte interface and reach the cathode, and decreases the performance. To address this issue, Whipple et al. [53] developed a fuel (methanol) tolerant catalyst for the oxygen electro reduction reactions. For this purpose, ruthenium-selenium chalcogenides (Ru_xSe_y) improved the cathode performance in the presence of methanol, by as much as 30-60% in the range of 1-7 M of methanol in comparison with the operation without methanol present in the cathode side. Oxygen transport at the cathode side due to the change in solubility and diffusivity can be considered as a possible explanation for observed increase in performance of Ru_xSe_y-base cathode in the presence of methanol. However, the absolute performance of the cell with Ru_xSe_y is lower than the cell with Pt cathode by a factor of 4 (~ 4 mW/cm² vs. ~16 mW/cm²). In this concept, fuel crossover will not be a concern anymore and the electrolyte can be eliminated as a separating stream. The elimination of electrolyte can decrease the size, weight and the complexity of the whole cell. Also, a much higher fuel concentration can be used so that the energy density of the cell can be improved.

4.3. Gas bubble formation

Since membraneless LFFCs exploit laminar flow regimes at very low Reynolds numbers, the interface of co-laminar streams are not affected by velocity fluctuations. But other mechanisms including bubble generation within the channel may disturb the interface leading to uncontrolled mixing of streams and performance degradation.

In addition to controlling the flow rate of the two streams to reduce diffusive mixing and fuel crossover, some methods to stabilize the co-laminar liquid-liquid interface have been proposed: utilization of a grooved microchannel geometry [30], introducing a third electrolyte stream between oxidant and fuel flows [67], using porous separator at the liquid–liquid interface [52], optimizing the channel geometry and tailoring the electrode geometry [59, 66, 70].

For a membraneless LFFC operating on H_2O_2 as oxidant oxygen evolution occurs in the channel due to the spontaneous decomposition of H_2O_2 [71]. Also, parasitic oxidation of H_2O_2 at the cathode side of a membraneless LFFC, running on a fuel stream like formic acid, can generate bubbles [30]. In addition to oxygen generation, carbon dioxide can be produced from oxidation of formic acid and methanol [72]. Choban et al. [49] argued that gas bubble formation, especially the formation of CO_2 bubble as a product of formic acid oxidation on the anode would hinder the performance of membraneless LFFC. The bubbles generated in the channel can degrade the performance by (i) decreasing the effective electrode area and (ii) the destruction of the liquid-liquid interface. Bubble can attach to the channel wall and grows resulting in blockage of the channel. In addition, generation and detachment of the bubbles/slug flow cause an intermittent flow field through the channel which can disturb the liquid–liquid interface [72]. In conclusion, crossover effects and a decrease of open-circuit potential are the consequences of bubble generation. Furthermore, to conduct a valid numerical simulation of membraneless LFFC, an understanding of bubble generation and the consequences of two-phase flow on cell performance must be taken into account.

To investigate the effect of bubble generation on a liquid–liquid interface, Shyu et al. [72],

visualized oxygen bubbles produced due to the decomposition of hydrogen peroxide in a microreactor with platinum-deposited electrodes. Two streams of water and hydrogen peroxide were introduced into the Y-shaped microchannel. Mixing index estimation was used in order to examine the effect of bubbles on the concentration distribution of the two streams.

Analysis of mixing and the flow visualization revealed that bubble generation depends on flow rate and the solubility of the species in a given media, concentration of the species and the cell current density. Rate of gas generation, for instance oxygen or carbon dioxide, is directly dependent on the cell current density. The produced gas (solute) can dissolve in the media (solvent). On the one hand, CO₂ formed in the channel dissolves in the flowing stream and is carried away from the system [49]. On other hand, gas bubble can appear in the stream if the liquid is saturated. In this case, a membraneless LFFC running at low flow rates is more prone to bubble generation.

Oxygen solubility in water (0.91 mg/100 mL) is much less than that of carbon dioxide (178.2 mg/100 mL). Thus, the presence of O₂ bubbles in microchannel has significant effects on the performance. Kjeang et al. [30] fabricated a membraneless LFFC using grooved microchannel in PDMS running on formic acid and hydrogen peroxide as fuel and oxidant, respectively. The aim of using grooved microchannel, as shown in Fig. 1(e), is to capture the oxygen bubbles formed by the parasitic electrochemical reactions over a cathode while stabilizing the co-laminar flow. Li et al. [37] reported that the O₂ bubbles generated from the parasitic decomposition of H₂O₂ resulted in the fluctuation of open-circuit potential. As a summary of design guidelines, the effect of gas solubility in both fuel and oxidant streams at a given flow rate and geometry must be taken into account to avoid or minimize bubble generation.

5. Fuel, oxidant and electrolytes

5. 1.Fuel types

Membraneless LFFCs have a wide option of fuels. With respect to fuel and oxidant selection, there are many fuels available including hydrogen (H₂) [34, 38, 73], methanol (CH₃OH) [26,47], ethanol (C₂H₅OH) [51] formic acid [28, 67], hydrogen peroxide (H₂O₂) [71] vanadium redox species [11, 74], sodium borohydride (NaBH₄) [51] and hydrazine (N₂H₄) [51].

Among aqueous fuels, formic acid and methanol with energy densities of 2.08 kWh/l and 4.69 kWh/l attracted more attentions for the use in membraneless LFFC due to the ease of access and well-studied electrocatalysis. A formic acid/O₂ fuel cell has a high theoretical electromotive force of 1.45 V while the corresponding value of methanol is 1.2 V.

Cohen et al. [28] tested a membraneless LFFC running by formic acid as fuel with platinum as catalyst to oxidize formic acid with combination of dissolved oxygen:

Using formic acid as fuel can provide a large open-circuit potential and high electrochemical efficiency [28]. The main disadvantage of formic acid is CO poisoning of the Pt-based catalyst.

Usually, vanadium redox couples dissolved in a supporting electrolyte such as sulfuric acid, V²⁺/V³⁺ as anolyte and VO²⁺/VO³⁺ as catholyte, are used to form all-vanadium fuel/oxidant system for membraneless LFFCs [11,27,45,68]. A membraneless LFFC can operate based on the following anodic and cathodic redox reactions and the standard electrode potential [45]

The advantages of this redox combination for microfluidic fuel cells are [18,45]: (i) providing the well-balanced electrochemical half-cells in terms of reaction rates and transport characteristics, (ii) having high solubility and relatively high redox concentration up to 5.4 M, (iii) having a high open-circuit voltage (up to ~1.7 V at uniform pH) due to the presence of large difference in

formal redox potentials, and (iv) utilization of bare carbon electrodes without precious metal catalyst to facilitate the reactions.

The energy density of a vanadium redox fuel cell is limited by the solubility of the vanadium redox species. To address this situation a new alkaline microfluidic fuel cell was demonstrated by Kjeang et al. [31] based on formic acid and hypochlorite oxidant. The reactant solutions are obtained from formic and sodium hypochlorite, both of which are available and stable as highly concentrated liquids, leading to a fuel cell system with high overall energy density. Formate (HCOO^-) oxidation and hypochlorite reduction were established in alkaline media on porous Pd and Au electrodes, respectively. The results indicate the rapid kinetics at low overpotentials while preventing the formation of gaseous CO_2 by carbonate absorption.

Brushett et al. [51] utilized 3 M hydrazine as fuel with a 0.5 M of sulfuric acid as electrolyte in an air-breathing flow architecture. For this hydrazine membraneless LFFC maximum power density of 80 mW/cm^2 was achieved at room temperature while the anode catalyst loading was 1 mg/cm^2 supported Pt and the fuel/electrolyte flow rates were 0.3 ml/min . Moreover, with the same operating conditions above, hydrazine was tested with oxygen delivery method at a flow rate of 50 sccm instead of quiescent air. No considerable improvement was achieved in peak power density and maximum current density indicating that this membraneless LFFC configuration is not restricted by oxygen transport.

This direct hydrazine acidic membraneless LFFC can be a promising micro-scale power source for applications where the safety is not a major concern. The theoretical open-circuit potential of a hydrazine/ O_2 fuel cell is 1.56 V . In addition, the end products of complete electro oxidation of hydrazine/ O_2 are nitrogen gas and water which can enable the hydrazine fuel cells to be eco-friendly zero-emission energy convertors [51]. Also, Brushett et al. [51] used 1 M sodium borohydride in 1 M KOH as fuel on Pt anode. However sodium borohydride with energy density of 9295 Wh/kg is unstable in acidic media, but highly stable in alkaline media. Peak power

density of 101 mW/cm^2 was recorded when both fuel and electrolyte stream (1 M KOH) flow at 0.3 ml/min with air-breathing cathode. This high performance is mainly credited to the improved electrocatalytic activity of Pt towards the oxidation of borohydride anions.

5.2.Oxidant types

Oxidant can be dissolved oxygen in aqueous form [26,37,48,49], air [25,46, 47, 51, 53], hydrogen peroxide [30,71], vanadium redox species [11, 27,74], potassium permanganate [44,67], and sodium hypochlorite [31].

Basically the cathodic half-cell electrokinetics is slower than the anodic one. The oxygen reduction reaction (ORR) is slow. Completion of ORR requires many individual steps and significant molecular reorganization, so the majority of activation overvoltage loss takes place at the cathode. At standard temperature and pressure (298 K, 1 atm) the exchange current densities (i_0) for oxygen reduction reaction (ORR) on Pt is six orders of magnitude lower than that of the hydrogen oxidation reaction (HOR). When the dissolved oxygen is used as oxidant, the slow electrokinetic reactions in cathode are coupled with low oxygen concentration resulting in low-power density. For improving the mass transport limitation of dissolved oxygen in electrolyte, alternative oxidants soluble at higher concentration than dissolved oxygen can be used.

Fuel cell designs using liquid oxidants have generally more power output. Choban et al. [49] replaced oxygen saturated in 0.5 M sulfuric acid by 0.144 M potassium permanganate as oxidant and used 2.1 M formic acid as fuel. The results showed that the cell operation using potassium permanganate developed a current density with one order of magnitude higher due to the higher solubility of potassium permanganate in aqueous media [49].

Li et al. [37], utilized saturated oxygen in 0.1 M H_2SO_4 solution as oxidant with 0.5 M HCOOH in 0.1 M H_2SO_4 solution as fuel. The maximum power density of 0.58 mWcm^{-2} was caused by insufficient supply of oxygen from the oxidant stream to the cathode.

Gaseous air was also used as oxidant in air-breathing configurations [25,46,47]. Since the

concentration of oxygen in air is four orders of magnitude higher than in aqueous media [46], the air cathode designs can provide a higher maximum power density and power output.

5.3. Electrolytes

In most membraneless LFFC designs, fuel and oxidant are dissolved in electrolyte and then usually introduced into the channel using syringe pumps. The main reason for adding electrolyte to the streams is to enhance the ionic conduction and to decrease the Ohmic losses across the distance between the anode and the cathode. As an example, by adding sulfuric acid to both streams in a membraneless LFFC, a source of protons closer to the cathode is provided and because of the proton consumption at the cathode, a gradient of protons is maintained [49]. Experimental results of Choban et al. [49] revealed that by using 0.5 M sulfuric acid as supporting electrolyte a maximum current density of 0.9 mW/cm^2 was obtained, while the maximum current density of the LFFC with water as electrolyte was just 0.2 mW/cm^2 at the maximum volumetric flow rate of 0.8 ml/min.

Lack of the membrane allows the cell to operate in acidic and alkaline media, as well as under “mixed-media” where the cathode is in acidic medium and anode is in alkali medium, or vice versa [26]. This flexibility enables the designer to tailor the composition of cathode and anode streams individually to optimize the individual electrode kinetics as well as the overall cell potential [26].

The pH of the electrolyte is effective on the reaction kinetics at the individual electrodes, and the electrode potential at which oxidation or reduction takes place [26]. Electrolyte is typically a strong acid or a strong base, such as sulfuric acid or potassium hydroxide which include highly mobile hydronium or hydroxide ions, respectively [18]. Typically, operation of fuel cell in alkaline media can lead to electro oxidation of the catalyst-poisoning carbon monoxide on the anode and the kinetics of ORR is improved at the cathode [26]. However, in membrane-based fuel cells, due to the potential of carbonate formation resulting in clogging the membrane, the long-

term stability is restricted and limits the use of these alkali-compatible membranes for liquid fuel cell operations [26].

Bruhsett et al. [51] examined the performance of air-breathing membraneless LFFC operated with ethanol and methanol under acidic (H_2SO_4) and alkaline (KOH) conditions. Methanol and ethanol showed improved open-circuit potential and maximum power density in alkaline media (1.2 V and 0.7 V, 17.2 mW/cm^2 and 12.1 mW/cm^2) compared to acidic conditions (0.93 V and 0.41 V, 11.8 mW/cm^2 and 1.9 mW/cm^2). The improved performance in alkaline media was caused by the enhanced kinetics of alcohol oxidation and oxygen reduction.

Choban et al. [26] investigated the acidic (H_2SO_4), alkaline (KOH) and acidic/alkaline media on the cell potential and power output of a membraneless LFFC running on 1 M methanol and dissolved oxygen. The results indicate that the process in both acidic and alkaline media was cathode-limited, and can be attributed to the low oxygen concentration in the solution. The oxygen solubility in acidic media was about 1mM while the oxygen solubility in alkaline media was approximately 25% lower resulting in earlier drop in performance in the I-V curve [26]. Also, there is no issue with carbonate formation in their work due to the immediate removal of any formed carbonates from the system by the flowing streams.

In the case of acidic anode stream combined with an alkaline cathode stream, the maximum theoretical OCP is 0.38 V, but an OCP less than 0.1 V was observed due to the overpotentials on the cathode and anode. In other words, the energy liberated in the methanol oxidation and oxygen reduction reactions is mostly used by water ionization reaction. In this configuration, the electrolytic reaction combined with a galvanic reaction is incapable of producing a large amount of energy [26].

In the case of alkaline anode and acidic cathode, the combination of two galvanic reactions in this configuration yields a desirable high theoretical OCP of 2.04 V. However, the practical OCP is 1.4 V due to the slow kinetics of oxygen reduction and methanol oxidation. Also the power

density of mixed media is higher than those obtained for all-acidic and all-alkaline membraneless LFFC experiments.

Most of the observed extra power density for the mixed media configuration is supplied by the electrochemical acid-base neutralization reaction, where protons are reduced on the cathode and hydroxide ions are consumed in methanol oxidation at the cathode. So, the consumption of H_2SO_4 and KOH must be taken into account while comparing the different membraneless LFFC configurations.

While the cell is running under alkaline anode with acidic cathode conditions, both OH^- and H^+ are consumed at the anode and cathode at a rate of six for each molecule of methanol. The maximum theoretical energy density (based on the reaction of 1 M of methanol with ambient oxygen, consuming six equivalents of H_2SO_4 and KOH) is 495 Wh/kg, much lower than the theoretical value for the all-alkaline and all-acidic LFFC in which only methanol is consumed (6000 Wh/kg) [26].

Hasegawa et al. [71] utilized the mixed media approach to operate a microfluidic fuel cell on hydrogen peroxide as both fuel and oxidant, in alkaline (NaOH) and acidic (H_2SO_4) media, respectively. This design produced a relatively high power density up to 23 mW/cm^2 . The drawback of this design is the spontaneous decomposition of hydrogen peroxide on the cathode and the associated bubble generation due to oxygen gas evolution that may disturb the co-laminar flow interface.

The overall reaction of this concept is:

which involves the disproportionate reaction of H_2O_2 together with the combination of H^+ and OH^- ions. The SO_4^{2-} ion neutralizes the Na^+ ion electrically at the acidic/alkaline bipolar electrolyte interface to allow the reaction of equation (19) to proceed continuously. Consequently, the products of this fuel cell type are water, oxygen, and salt.

6. Challenges and opportunities for further development

The papers published between 2002 and 2010 revealed that extensive improvements have been achieved in the design and performance of membraneless LFFC.

The performance of a membraneless LFFC is comparable with direct methanol PEM fuel cells. For example, the maximum power density of a membraneless LFFC running by 1 M methanol in 0.5 M H₂SO₄ as acidic electrolyte with air-breathing electrode can be on the order of 15 mW/cm² which is similar to the corresponding value of a micro direct methanol fuel cell (μDMFC) with air-breathing cathode.

Power density is coupled with fuel/oxidant flow density. To have a fast replenishment of depletion boundary layer-specifically on planar electrodes- and removal of reaction products such as bubbles, flow rate should be increased in expense of low fuel utilization in a single pass.

For practical applications, the power of a single cell is not adequate. Because of the design constraints and the laminar nature of the streams in a cell, enlarging the cell dimension is not practical. Instead, an array of interconnected cells in planar and vertical configuration can be a suitable scheme for reasonably high power generation.

The main challenging obstacle for stacking is the low fuel utilization in a single pass and mixing of the fuel/oxidant or fuel/electrolyte. In this case, implementation of a recirculation system becomes complicated. Unlike membrane-based fuel cells, a dead-end anode can't be considered to increase the fuel utilization in single pass.

A small fuel cell can be a power source for stationary devices where the plug-in power is difficult to implement. The devices are for example wireless sensors for biological and environmental sampling, or sensors for motion detection and monitoring at borders [4]. For some portable applications such as Lab on Chip devices, a membraneless LFFC can be a potential power source as well. In such applications, the devices may have two different power demands: (i) low-power-demand mode where the device is in sleep mode, for example a sensor is in monitor-style mode to

record biological parameters, and (ii) high-power-demand mode where the device requires high power, for example the sensor needs to transmit data, or species in a Lab on Chip are to be transported by electroosmosis [75]. To meet the energy requirements of both low-power-demand mode and high-power-demand mode, a fuel cell can operate constantly during the sleep mode in the steady state operating conditions to recharge a secondary battery for the burst-power occasions.

The major developments for practical applications and commercialization revolve around the increment of power density at low flow rates to achieve high fuel utilization per single pass which increases the volumetric power density. To achieve high power density, mass transport limitation losses, electrochemical kinetic and the Ohmic losses should be addressed. At low flow rates, fuel crossover become a major issue which results in broadening the zone of diffusive mixing. Flow-through electrodes in combination with new flow configuration can provide a venue towards improved fuel utilization and power density. In addition, by improving fuel utilization, fuel concentration at the interface of the co-laminar flow decreases and fuel crossover alleviates. Fabrication of new electrodes can benefit from microfabrication techniques to enhance the surface area for electrochemical reactions. However, this process can increase the total fabrication cost.

If selective catalysts for electro oxidation and electro reduction reactions are explored, mixing of fuel and oxidant will be a less concern. Bubble generation over anode due to oxidation of methanol or formic acid can be used as passive pumping scheme. By directional growth and selective venting of CO₂ bubbles through a nanoporous membrane, a micro pumping mechanism is provided that can be used for self-circulation [76].

Amongst the designs of membraneless LFFCs available in the literature, membraneless LFFC with air-breathing cathode seems to be a promising design for some practical operations.

Oxygen transfer rate can be improved through a thinner GDE. Fuel utilization can be improved by exploiting a flow-through anode which has not been addressed yet. The typical flow rate of

fuel/electrolyte ranges from 100 to 300 $\mu\text{l}/\text{min}$. At operations with high fuel utilization, the fuel/electrolyte flow rates can be decreased to a very low value.

Equation (20) indicates that as flow rates (Q) decreases, pumping power (W) for fuel and oxidant or electrolyte is decreased in a given geometry [77]:

$$W = \frac{12\mu QL}{wd^3}Q \quad (20)$$

where L and d are the length and the depth of the channel, U is the mean flow velocity, and μ is the fluid viscosity. For a membraneless LFFC with air-breathing cathode built in a rectangular channel with width, depth and length of 3.3 mm, 2 mm and 30 mm, total flow rate of 600 $\mu\text{l}/\text{min}$ [51], and viscosity of 0.9 mPa .s, the minimum required pumping power at a temperature of 25 $^{\circ}\text{C}$ is 1.2 mW.

The maximum output power of this cell at a flow rate of 600 $\mu\text{l}/\text{min}$ (300 $\mu\text{l}/\text{min}$ of fuel and 300 $\mu\text{l}/\text{min}$ of electrolyte) is 25 mW at 0.3 V. The required pumping energy at this given flow rate is less than 5% of the maximum power output, but implementing a micropump for injection of fuel and electrolyte adds too much complexity to the system design. The suitable solution for fuel/electrolyte injection can be a fuel/ electrolyte cartridge with a flow regulator. The cartridge can have a piston-spring configuration, and the spring can be pressed manually once. While the spring is decompressed gradually, a pressure-driven flow is supplied and adjusted by the regulator.

7. Conclusions

This review paper discusses the design, fabrication, and the performance of membraneless LFFCs. The data and information extracted from papers published between 2002 and 2010 revealed that extensive improvements have been achieved in the design and performance of membraneless LFFC. But there is a big potential for research in this field and new advances can be explored in coming years. High performance can be achieved by paying careful attention in design considerations in view of the coupled mass transport to reactive sites and the

electrochemical kinetics. Ohmic losses should be decreased by optimizing the spacing between electrodes and enhancing the conductivity of electrodes and aqueous electrolytes.

Among the three designs of membraneless LFFCs available in the literature, membraneless LFFC with air-breathing cathode seems to be a promising option for practical use. Commercialization of membraneless LFFC imposes the scale up of the power by stacking of the single cells. Stacking needs space-efficient handling of fuel and oxidant through a micro-fluidic network as well as efficient interconnection. There is a huge potential for the integration of a membraneless LFFC with other microfluidic devices such as microvalves and fuel cartridges to build a standalone fuel cell system. In this case, a membraneless LFFC can be used for empowering Lab on Chip devices or off-the-grid microdevices or a potential sensor for long operational times.

Acknowledgment

SAMS would like to acknowledge the scholarship from A*STAR (Agency for Science Technology and Research) to pursue postgraduate studies.

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Table 1 – Performance of LFFCs running on formic acid or methanol [18].

Design	Fuel/Oxidant	Electrolyte	Electrode/flow structure	Maximum current density (mA/cm ²)	Maximum power density (mW/cm ²)	Design features
Choban et al. [26]	Methanol (1 M) Dissolved O ₂	Sulfuric acid or Potassium hydroxide (1 M)	Flow-over	40	12	Mixed media operation
Choban et al. [48]	Methanol (1 M) Dissolved O ₂	Sulfuric acid (0.5 M)	Flow-over	8	2.8	–
Cohen et al. [28]	Formic acid (0.5 M) Dissolved O ₂	Sulfuric acid (0.1 M)	Flow-over	1.5	0.18	Stackable microchannels
Choban et al. [49]	Formic acid (2.1 M) Dissolved O ₂	Sulfuric acid (0.5 M)	Flow-over	0.8	0.17	–
Li et al. [37]	Formic acid (0.5 M) Dissolved O ₂	Sulfuric acid (0.1 M)	Flow-over	1.5	0.58	Laser-machined
Morales-Acosta et al. [50]	Formic acid (0.1, 0.5 M) Dissolved O ₂	Sulfuric acid	Flow-over	11.5	3.3	Pd/MWCNTs as catalyst
Salloum et al. [44]	Formic acid (0.04 M) Potassium permanganate (0.01 M)	Sulfuric acid (0.5–1 M)	Flow-through	5	2.8	Sequential radial flow
Kjeang et al. [31]	Formic acid (1.2 M) Sodium hypochlorite (0.67 M)	Sodium hydroxide (2.8 M)	Flow-through	230	52	3D structure of electrodes
Jayashree et al. [46]	Formic acid (1 M) Air	Sulfuric acid (0.5 M)	Air-breathing	130	26	–
Jayashree et al. [47]	Methanol (1 M) Potassium hydroxide (1 M) Air	Sulfuric acid (0.5 M)	Air-breathing	120	17	–
Brushett et al. [51]	HCOOH (1 M) Air	Sulfuric acid (0.5 M) or potassium hydroxide (1 M)	Air-breathing	130	26	–
Hollinger et al. [52]	Methanol (1 M) O ₂	Sulfuric acid (1 M)	Air-breathing	655	70	Methanol@80 C with O ₂ feed to the cathode
Whipple et al. [53]	Methanol (0.1–15 M) Air	Sulfuric acid (0.5 M)	Air-breathing	62	4	Using Ru _x Se _y as methanol-tolerant catalyst for cathode

Table 1

Table 2 – Design features of three different electrode architectures with maximum power density running by formic acid or methanol.

Reference	Maximum power density (mW/cm ²)	Design features and comments
Flow-over electrode Choban et al. [26]	12 at flow rate of 3 ml/min per inlet flow	Side-by-side streaming, Y-shape geometry, 29 mm channel length, 1 mm channel height and 0.75 mm channel width, Pt/Ru and Pt black nanoparticles in Nafion-based ink solution applied to graphite plate as anode and cathode, Fuel utilization <10%.
Flow-through electrode Kjeang et al. [31]	52 at 0.4 V and flow rate of 60 µl/min per inlet	Side-by-side streaming, T-shape geometry, 12 mm channel length, 0.3 mm channel height, 3 mm channel width, electrodeposited Pd and Au on carbon paper strips to make flow-through anode and cathode, Fuel utilization of 85% at peak power density and 100% at lower voltages.
Air-breathing electrode Hollinger et al. [52]	70 at flow rate of 0.3 ml/min per inlet	Vertically layered streaming, T-shape geometry, 48 mm channel length, 3.3 mm channel width, Pt/Ru and Pt nanoparticles in Nafion-based ink solution brushed on carbon paper as electrodes, graphite plates as current collectors, implementation of a nanoporous separator at the fuel–electrolyte interface, running at 80 °C with O ₂ supply of 50 sccm, hot pressed thin film of Nafion over cathode to alleviate fuel crossover effects.

Table 2

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11