World Journal of Engineering Research and Technology
WJERT
www.wjert.org
SJIF Impact Factor: 5.218

MICROFLUIDICS DEVICES APPLICATION IN ENERGY CONVERSION

***[1]Ran Zhou and [2]Mark Parra**

[1]Assistant Professor. Department of Mechanical and Civil Engineering, Purdue University Northwest. Hammond, IN, USA.

[2]Graduate Research Assistant. Department of Mechanical and Civil Engineering, Purdue University Northwest. Hammond, IN, USA.

Article Received on 18/01/2019 **Article Revised on 09/03/2019** **Article Accepted on 30/03/2019**

***Corresponding Author**
Ran Zhou
Assistant Professor. Department of Mechanical and Civil Engineering, Purdue University Northwest. Hammond, IN, USA.

ABSTRACT

In recent years, greenhouses gas emissions keep increasing and bring severe impact on natural environment. Renewable energy sources has become more and more important to reduce overall carbon dioxide emissions. Microfluidic energy conversion devices have been found a possible solution to greenhouse issue. Microfluidics energy conversion devices are in their beginning stages but show promising hope. Throughout this manuscript, we have brought to light novel devices that increase overall performance of microfluidic energy conversion devices. The most enticing feature of these devices is their Laboratory-on-Chip capabilities where all functionalities of an entire laboratory are integrated onto a single microfluidic chip, so it can reduce volume of samples and reagents. Here we introduce most important three methods to convert energies in the microscale. These include membraneless electoylyzers, two phase flow fuel cells and vapor fed hydrogen generators.

KEYWORDS: Microfluidics; Energy Conversion; Membraneless Electoylyzers; Fuel Cells; Vapor Fed Hydrogen Generators.

1. INTRODUCTION

Greenhouses gas emissions keep increasing in recent years, so renewable energy sources is important to reduce overall CO2 emissions.[1,2] A possible solution to this crucial issue is

deployable microfluidic energy conversion devices. Since their inception in the early 1990's, the science of microfluidics has come to be known as the study of systems that process or manipulate small amounts of fluids. 'Small' means 10-19 liters while utilizing channels with just hundreds of micrometers. Exploiting physical and chemical properties on the microscale presents multiple advantages including reduced volume of samples, chemicals and reagents, global fees of applications, and overall experiment durations. The most enticing feature of these devices is their Laboratory-on-Chip capabilities where all functionalities of an entire laboratory are integrated onto a single microfluidic chip. Because of these advantages, multiple applications such as PH control and drug administration has exploited them. However, microfluidic applications in the energy area are relatively new and have only started to be explored. Currently the lack of deployable and economical storage mechanisms impedes their ability to become the leading supplier of energy in the world, which seems quite possible via hydrogen for excess energy storage, due to it being a convenient fuel and its high-power density.[3]

Currently there has been great interest in microfluidic membraneless electrolyzers where the electrolyte flows in-between electrodes and fluid products are attracted to their respected electrode. While microfluidic fuel cells based on purely liquid flow have been investigated a similar device using two-phase flow comprised of annular gaseous H2 and O2 in liquid, electrolytes has been shown to relax mass transfer limitations and increase energy conversion efficacy. Vapor fed hydrogen generators is a novel idea that has been demonstrated by producing hydrogen from atmospheric humidity. Also, a novel photothermic reactor has been developed that utilizes sunlight as a shared source for both heating and catalysis, which takes advantage of a larger part of the solar spectrum. This reactor can also be used to feed membrane-less electrolyzer. Even though these devices are on the microscale, they are scalable and can reach power conversion in the megawatts. We will briefly review the mass transport phenomena in electrochemical reactors using water electrolysis as the model reaction.

2. MATERIALS AND METHODS

Here we introduce most important three methods to convert energies in the microscale. These include membraneless electoylyzers, two phase flow fuel cells and vapor fed hydrogen generators.

2.1 Membraneless electrolyzer

An essiental part of a water electrolyzer, in the microscale, has been an ion conductive membrane. The standard proton conducting membrane has been Nafions in both academic and industrial settings since the 1960s. It has been accepted by researchers even though it has a high price, limited lifetime, and disadvantages when used with strongly acidic pH values. Besides this, its water management aspect can be seen as a litmitation because the mebrane must be moist but not completely saturated in water. If it is to dry or to wet the systems, overall power output will drop significantly. Due to waters saturation temperature, higher operating temperatures are limited that would increase device efficiency.

Membraneless electroylzers utilitzes boyancy forces to separate the liquid electrolyte products of H2 and O2 before they come into contact with their respective electrodes. They include enhanced functionality, compared to their membrane counter parts, whereby doubling as a fuel cell to produce electricity when used in reverse. Two types currently exist as seen in Figure 1. The fluid electolyte velocity gradient can be used in concordance with the Segre´-Silberberg effect to keep bubbles pinned to the electrode surface where they originate from.[6] The first Type I membraneless electrolyzer was demonstrated in 2015 with the capability of non-flammable hydrogen production across the pH scale.[2] Intrestingly enough, these results were replicated by a 3D printed version of the same membraneless electrolyzer, adding the benefit of limiting processing times and device complexities.[7] Type II, on the other hand, employs mesh electrodes that allows the liquid electolyte to flow through them as seen in Figure 1. Two circlular mesh electrodes opposite of one another allow for circumferential electrolyte flow in opposing directions.[8]

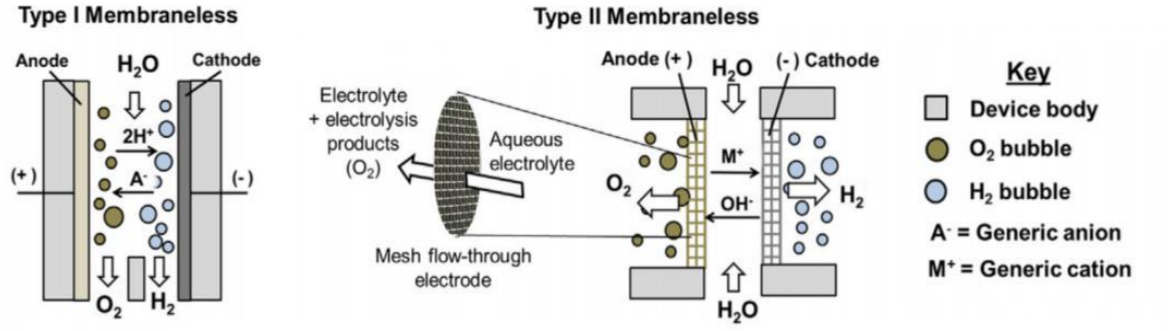

Figure 1: Schematics of Low-Temperature Membraneless Electrolyzer Technologies.[9]

Membraneless electrolysis schemes can address the challenges of polymer electrolyte membrane (PEM) electrolyzer. They also lead to a reduced weight, size, and overall cost

compared a convention membrane electrolyzer.[6] In general, membraneless electrolyzers can be developed with only three componets - cathode, anode, and cell body. This is much less than a traditional PEM cell which could have at least serval times the number of componets. All in all, due to the simplicity of the design, capitol cost are reduced through lower material and assembly costs. Simplicity of design also gives way to alternative manufacturing technologies to allow oppertunities for rapid prototyping and fabrication.[3,4] 3D printed membrane electrolyzers have been shown to achive efficiencies using acidic and alkaline solutions.[6] While a membraneless 3D printed cell body has also been demonstrated being used for a standalone H2 production in seawater.[8]

Membraneless design.[2,4,5] is unlike membrane based devices because the ionic conduction through the electolyte gap is largely unaffected by electrolyte ions and pH. Using a neutral pH liquid electolyte is attractive because cathodes and anodes will last longer and not be corroded by strong acidic liquid electrolytes. In this sense, overall material cost could be reduced by using inexpensive catalysts and assembly materials.

An approach has been reported to use electrolysis to disinfect waste water, which reduces 95% of the chemical oxygen demand and ammonium ion in 6 hours.[9,10] Membraneless electrolyzers can become a disruptive technology in the field of renewable hydrogen production due to their agnostic nature. They can be used in harsh environments and even with other electrolysis processes such as CO2 electrolysis.[10] They have been shown to produce acid and bases from a brine solution.[11] Conversely, a planar membraneless microchannel fuel cell device has been proposed to use formic acid as fuel and oxygen as oxidant with power densities.[12] A significant driver of low power densities is due to the shear distance that ions need to travel. Usually the electrode gap of membraneless electrolyzer can be less than 500 μm to several millimeters.[1,10] while a PEM electrolyzer membrane will range anywhere from 100 μm to 200 μm.[13]

Membraneless electrolyzers also face the problem of producing H2 and O2 products with high purity safely. PEM electrolyzers have the advantage of a barrier between product gases and have been shown to produce high product purities of 99.99%.[14] This is unlike membraneless electrolyzers that cannot keep big pressure drop. They can however operate using a pressurized liquid electrolyte,[15] in effect eliminating the need to utilize compressors to efficiently store products. In this respect, recently a system was demonstrated to produce H2 and O2 at 200 atm using electrodes made from AISI 321 Stainless Steel without using

compressors to facilitate storage.[16] H2 purity produced by membraneless electrolyzers has been to found to be well outside explosive limits, above 99%.[2,8,9] Also present safety hazard is electrical arcing in-between electrodes especially when a large voltage is applied. Ultimately, membraneless electrolyzers are implemented into real-world application. In general, scaling can be achieved through a parallelization approach.[5] This can be done by lengthening the device and/or given a large electrode gap and operating at lower current densities to increase electrode size. A type II device electrodes was able to achieve a current density of 508 mA cm−2 at 2 VDC, however the maximum H2 quality was 90.5% and O2 was 75.7%.[22] This is a stark quality degradation compared to previous results of 99.83% maximum H2 quality.[8] Such gas quality reductions may be due to an increasing flow velocity, which shortens residence times that enable of gas/liquid separation.[17] Parallelization is also a possible strategy. More devices are added with manifold designs and fluidic connections can become complicated quickly. A simple 3D printed modular 3-cell stack membraneless electrolyzer design at 100 mA cm−2 has been demonstrated in this respect.[10] And also, a planar membraneless microchannel fuel cell was also able to be stacked to increase power generation.[12]

2.2. Fuel cell based on two-phase flows

Although water electrolysis was discovered in 1800, the inverse process of fuel cells were not realized untill 1838, initially being described as a gas battery.[18] Since its initial concept, fuel cells have started to become a dominate player in todays energy arena due to their high power density, high efficiency, fast startup time, low operating temperature, and easy and safe handling characteristics.[19] They can be found in a number of different applications such as vehicles, vacuum cleaners, mobile phones, banks, police stations, and hospitals. Fuel cells in the microscale however have yet to be seen such exposer because they are a relativly new energy conversion device. They have great potential to be a promising power source for consumer electonics due to their intrinsically light weight and compact design. And also, it is advantageously compatiable with semiconductor manufacturing processes.[16]

In an effort to increase microfluidic fuel cell device performance, two-phase flow fuel cells have recently been investigated. New devices were created by the integration with distributed sensing elements to fully understand the flow behavior in microchannels.[20] Improvements in water management and gas routing in microfluidic fuel cells have been studied,[21] but currently limited microfluidic two-phase flow fuels cell devices have been developed and

studied. In any case, such a device would need to keep H2 and O2 gas streams separated and to keep the streams completely imersed in an liquid electrolyte. In addition, it would be important to keep the velocity of the gas streams relativily high to minimize mixing,[2] meaning that gas cross over would be negligible since it would only occur from diffusion.

A membrane-less microfluidic fuel cell device has been developed that reduces mass transport limitations.[16] It keeps the H2 and O2 streams of gasseous bubbles seperated in their own microfluidic channels until they meet at a shallow ionic bridge, as seen in Figure 2. Through the microchannel paths, the bubbles become elongated and are surrounded while they are still surrounded by the liquid electrolyte. Gases then are able to diffuse to the surfaces of thin platiumum electodes that cover the top of each gas channel. In this way, a thin liquid film is able to wet the channel walls where bubbles continuously feed the liquid film that seperates the gas streams from the electodes. Single-phase and two-phase conditions were able to be studied using the same device by blocking of the gas inlet tubes and saturating the the electrolytes with hydrogen and oxygen. Therefore, this device can reduce mass transport limintations and increase efficiency.

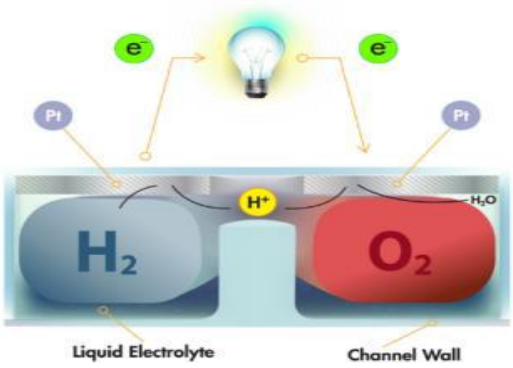

Figure 2: Two-phase flow concept in a membrane-less microfluidic fuel cell.[16]

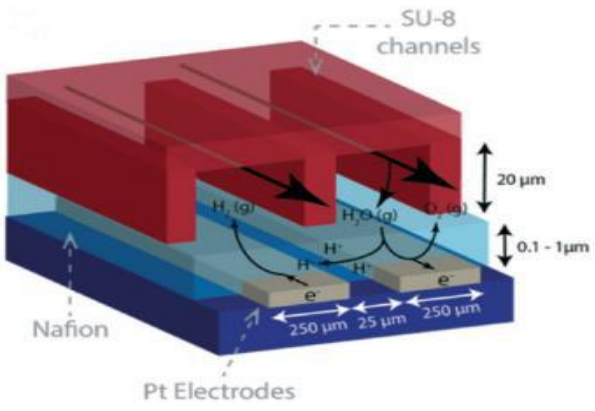

Figure 3: Diagram of spiral geometry device geometry.[24]

2.3. Vapor fed hydrogen generator

Vapor fed hydrogen generators have been created in the past but no so much on the microfluidic scale. This devices requires many operating points including a solid state ion condutor to transport all ionic currect between the reaction sites. The solid electolyte and electrodes have to be in direct contact with eachother. The electrode surface production rate needs to be satisfied by a product diffusive flux. H2 and O2 saturation levels must not be attained to prevent delaminating the electrolyte by bubble nucleation. In Figure 3, a spiral geometry was used to increase areal coverage and allow maximum coverage of the electrode. In effect, it allows for the separation of hydrogen and oxygen fluid streams to prevent back-diffusion of H2. This architecture is at its core, which is fundamentally different from most membrane electrode assemblies and proton exchange polymer membranes. In membrane electrode assemblies, a parallel ionomer membrane seperates the nanostructed catalyst layers. Also the cross section of a less than 1 μm thick ionomer film is used convey ionic current. In this device, the ionic flux production rate of the catalyst layer equals the ionic flux through the membrane. And the ionomer is exposed to an ionic current density which is 125 times greater than that at the catalyst's surface.

3. CONCLUSION AND DISCUSSION

Microfluidics energy conversion devices are in their beginning stages but show promising hope. Throughout this manuscript we have brought to light novel devices that increase overall performance of microfluidic energy conversion devices. Membraneless electrolyzers are shown to reduce device complexity by which design capital costs are cut by lowering weight, size, and parts compared with a convention membrane electrolyzer.[6] Furthermore, simplified manufacturing such as 3D printing can be considered to enhance functionality. In addition, they can be used in harsh environments and even with other electrolysis processes such as CO2 electrolysis, due to their agnostic nature.[10] The only drawback, besides safety concerns of keeping H2 and O2 products separate, is that currently peak power densities are restricted to less than 1 mW/cm2.[16] This is similar when looking at microfluidic fuel cells. However, it was found to increase performance when introducing a two-phase flow comprised of gaseous products with liquid electrolyte. Although this type of device is more complicated due to an increase of channels and tubes, its performance gains out way such complexity. And also, a novel approach to water-splitting is explored that utilizes electrolysis to split atmospheric water vapor which produces hydrogen. Another novel device includes the introduction of a photothermal reactor that captures 93% of sunlight compared to devices that could only

capture 7% using TiO2 as the photocatalyst. The reaction chamber is heated through non-UV sunlight and the pollutants in water photocatalytically decay by using UV sunlight. The performance increase 82% over the same photoreactor.[22] It aids in cooling of the solar cell thus improving performance.

What's more, several processes have been identified to limit mass transport effects and increase efficiency through processes in the boundary layers of water electrolysis. The production of hydrogen through electrochemical means is not economical due to the current cost of electricity.[23] These devices show increases in efficiencies and higher power densities than previous generations of devices, which has been brought along through a deeper understanding of their mass transport limitations. In this way, the continued study of multiphase flow electrochemical reactors is a priority to meet cost-effectiveness requirements for adoption.

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