Microbial Fuel Cells

Bruce E. Logan
The Pennsylvania State University

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Microbial Fuel Cells

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To Maggie, Alex and Angela,
for their love and support

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Preface

This book is made possible by work performed in my laboratory as well as experience gained through numerous collaborations that were started only a few years ago, but the roots of my education in the area of exogenous electron transfer go back two decades. I first began to learn about iron reducing bacteria from Bob Arnold and his group in 1986, when Bob and I were both assistant professors at the University of Arizona. Bob was an early pioneer in the area of solid iron oxide reduction by bacteria, and I am grateful to Bob and his students (particularly Flynn Picardal) for sharing their work and thoughts with me over the years about these fascinating bacteria.

In the fall of 2002, I started work on microbial fuel cells (MFCs) and was fortunate to work with Hong Liu, a postdoctoral researcher with my group at that time, as she made essential creative and intellectual contributions to our laboratory's work on MFCs. Through her efforts and excitement for this topic, work in my laboratory advanced at a rapid pace and we made many interesting discoveries over a short period of time. In the years since I started working on MFCs, I have been privileged to work with a number of talented researchers, but I especially appreciate having worked with the following students and researchers in my laboratory: Shaoan Cheng, Booki Min, JungRae Kim, SangEun Oh, Jenna Heilmann Ditzig, Yi Zuo, Douglas Call, Valerie Watson, Rachel Wagner, Farzaneh Rezaei and Defeng Xing. My own research efforts have always focused on the biophysical interface, and so I have relied on collaborations with others having greater expertise in chemistry, biology, molecular biology techniques. I am grateful to Tom Mallouk at Penn State for all his patient explanations of fuel cells and electrochemistry, and the assistance of his student Ramna Ramnarayanan. I particularly appreciate collaborations with Jay Regan and his group at Penn State, as their expertise and knowledge have been absolutely essential for work that has emerged from Penn State.

Collaborations outside of Penn State have been critical for advancing the field of MFC research. In 2003 I spent a sabbatical at the University of Newcastle upon Tyne, and I benefited from conversations and work with Ian Head, Tom Curtis, Cassandro Murano, and Keith Scott. Collaborations have continued with this group through the efforts of Eileen Wu, who joined my research group for several months. I am continuing to benefit

from additional collaborations with Yuri Gorby (J. Craig Venter Institute), Ken Nealson and Orianna Bretschger (University of Southern California), Tim Vogel, Jean-Michel Monier (Ecole Centrale de Lyon, France), Yujie Feng and Aijie Wang (Harbin Institute of Technology, China), Kazuya Watanabe and Shunichi Iichi (Marine Biology Institute, Japan), Kyeong-Ho Lim (Kongju National University, Korea), and many others.

This book really represents the next stage of evolution of a paper written in 2006, with co-authors Peter Aelterman, Bert Hamelers, René Rozendal, Uwe Schröder, Jurg Keller, Stefano Freguia, Willy Verstraete, and Korneel Rabaey. The chapters of this book on voltages and power are based on a section of that paper originally crafted by René and Bert, with additional contributions from Uwe and Korneel. I especially appreciate the extra effort and continued discussions with René on thermodynamics, power calculations, and MECs, and with Kornell on MFCs. Each of the chapters in the book has been improved by comments provided by a number of different colleagues, and I thank especially: René Rozendal, Ian Head, Nathan Lewis, Annemiek ter Heijne, Korneel Rabaey, Ken Nealson, Uwe Schröder, Song Jin, Jurg Keller, Lenny Tender, and Denny Parker.

I thank collectively everyone I mentioned above for their help in making a book like this possible. I look forward to continued rapid developments in the exciting areas of MFCs, MECs/BEAMRs, and bioenergy production.

BRUCE E. LOGAN

State College, Pennsylvania
September 2007

CHAPTER 1

Introduction

1.1 Energy needs

There are over six billion people on the planet with 9.4 billion projected for 2050 (*Lewis and Nocera* 2006). Fossil fuels have supported the industrialization and economic growth of countries during the past century, but it is clear that they cannot indefinitely sustain a global economy. Oil will not appreciably run out for at least 100 years or more, but demand for oil is expected to exceed production from known and anticipated oil reserves ten or twenty years from now, or within the 2015 to 2025 time frame (*Rifkin* 2002). This may seem distant to many consumers and businesses that rarely plan for more than three to five years in the future, but this is a very short time frame for society as a whole. Planning a single section of an interstate highway in a city, for example, can take ten years or more. The infrastructure changes needed to address our global energy needs will be far more extensive and will likely require changes not only to our infrastructure but also to our lifestyle. Changes will affect everything from home heating and lighting, to where we prefer to live and work and how we get there. The costs of energy and how much energy we use will come to dominate our economy and our lifestyle in the coming decades.

The total annual energy consumption in the US is ~100 quads of energy (100 quadrillion BTU = 10^{15} BTU), or 1.1×10^{15} J, which is a continuous consumption rate of 3.34 TW (1 TW = 10^{12} W). On a global scale, energy use is 13.5 TW (*Lewis and Nocera* 2006), Thus, the US uses about 25% of the world's energy despite having only 5% of the world's population. Energy in the US is derived from a number of sources, but most are fossil fuels (Fig. 1.1). Approximately 18% of this energy (600 GW) is generated as electricity at power plants that vary greatly in size, with a typical large power plant producing ~1 GW. Power plants are 33% efficient, so energy used to make this electricity is larger by a factor of three.

If we assume a base of 300 million people in the US, each person in the US consumes on average 11.1 kW, or 97 MWh per year. This is not a level of energy utilization that we see in our daily life as much of this energy is used for manufacturing and transportation or is lost as heat in various energy conversion and utilization cycles. At a more local level, an average US house uses 1.22 kW while a home in British

Microbial Fuel Cells. By Bruce E. Logan

Columbia, Canada uses 1.5 kW (non-electric heating) to 2.5 kW (electric heating) (*Levin et al.* 2004). In comparison, 500 gallons of gas is annually used per person in the US, or an energy equivalent of 2.1 kW.

How much energy will we need in the future? One estimate of population growth, coupled economic growth at current levels, puts a global demand of 41 TW in 2050 at current energy growth rates. However, considering anticipated energy trends, a more reasonable projection is 27 TW by 2050 and 43 TW by 2100 (*Lewis and Nocera* 2006).

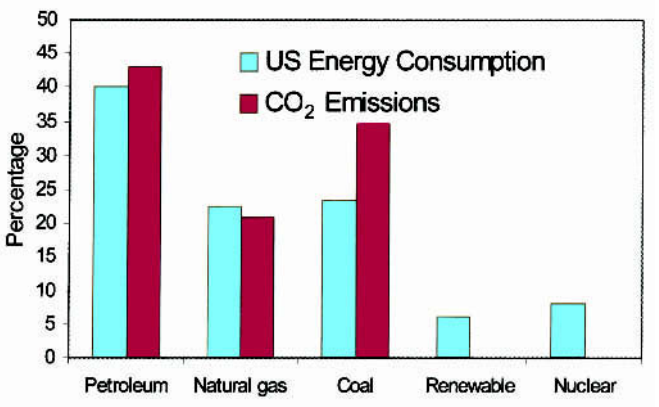

Fig. 1.1 Percent of US energy (98.5 Quad, 2003) by source and CO_2 emissions (5.772×10^9 metric tons. [From *Shinnar and Cintro* (2006). Reprinted with permission from AAAS.]

1.2 Energy and the challenge of global climate change

There is no "magic bullet" for meeting our current or future energy needs. While oil, natural gas, and coal are the main methods for energy production today (Fig. 1.1), this cannot continue into the future. When the US had its first oil crisis in the 1970s due to demand exceeding production, the solution was simply to find other sources of oil. However, finding new sources of oil, increasing the efficiency of extracting oil from existing source, or using other fossil fuels such as tar sands and shale oil will not address an equally challenging task of addressing climate change. There is no question that the release of stored carbon in fossil fuels is increasing the concentration of carbon dioxide in the atmosphere, with increases from 316 ppmv in 1959 to 377 ppmv in 2004 (Fig. 1.2A). By 2100, it is estimated that CO_2 concentrations will reach anywhere from 540 to 970 ppmv. Without substantial changes to our energy production methods, we will have greatly exceeded any historic level of CO_2 concentrations in the atmosphere. Global CO_2 accumulation over the next 40–50 yr will persist for the next 500–2,000 yr, and thus even the current levels of CO_2 are not likely to soon change. Global mean temperatures have already risen above pre-historic levels (Fig. 1.2B), resulting in melting of glaciers and rising sea levels.

The insufficient availability of oil and natural gas could be augmented by other fuels, such as coal, coal tars, oil shales, and methane hydrates. However, if we obtain energy from these sources using conventional technologies, we will release additional CO_2,

exacerbate environmental damage, and accelerate global climate change. Carbon capture and sequestration could be used, but this will continue to add to releases produced by other fuels. Clearly, we would need a very efficient method of carbon sequestration. We would need to develop a method that did not leak CO_2 into the atmosphere at an average rate (globally!) of more than 1% over centuries (*Lewis and Nocera* 2006). Of course this approach requires that all countries that release CO_2 are equally committed and effective in carbon capture and sequestration.

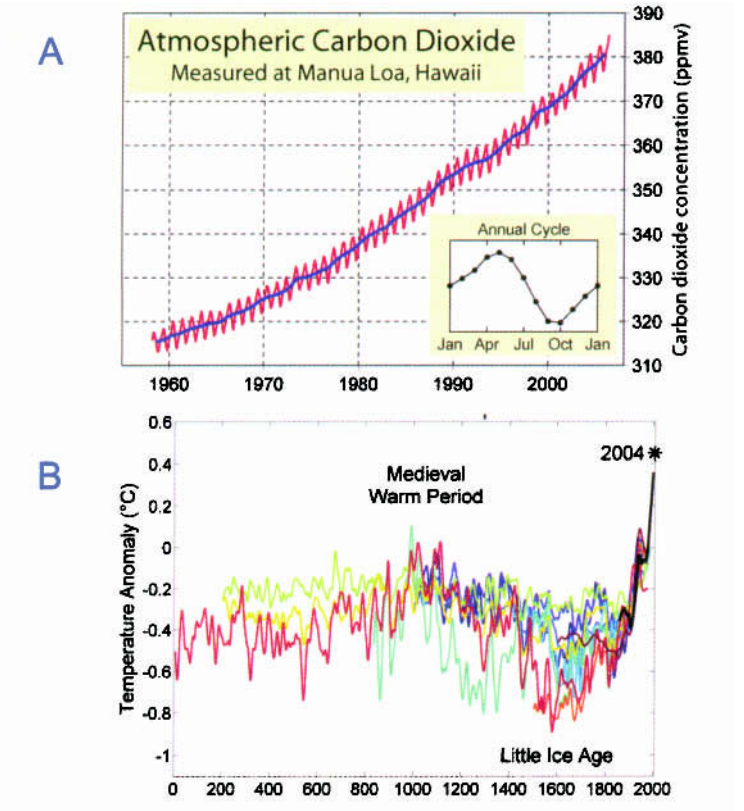

Fig. 1.2 (A) CO_2 concentrations in the atmosphere measured at Manua Loa (*Wikipedia-Contributors* 2007a); (B) temperatures relative to historic levels (*Wikipedia-Contributors* 2007b).

Our greatest environmental challenge is to simultaneously solve energy production and CO_2 releases: We must develop a whole new energy platform that produces sufficient energy while at the same time reduces CO_2 emissions. Our goal must be to meet 2050 energy needs on a carbon neutral basis.

Nuclear fission alone is not the answer. The expected availability of uranium is estimated to produce only 100 TW-h of electricity, and thus if 10 TW of power was obtained from nuclear energy the supply of uranium would be depleted in less than a decade. Moreover, we would need to build a new 1 GW plant every 1.6 days for the next 45 years (*Lewis and Nocera* 2006). This scenario doesn't even address the environmental

and human damage caused by uranium mining, or the lack of a safe, long-term solution for the storage of nuclear waste.

Solar energy is ultimately the long-term solution, but it all depends on how we harvest this source of energy. We currently use in 1 hour the energy of sunlight (4.3×10^{20} J) that strikes the planet each year. The sun does not shine all day, nor does it shine equally in all regions. Thus, solar panels can help with daytime electricity needs, but it will not serve as a primary source of energy throughout the day and night without efficient methods of energy storage. Water electrolysis to produce hydrogen is a useful approach as electrolysis can be quite efficient, and regeneration of electricity in hydrogen fuel cells could approach 80% compared to 50% currently achieved (*Grant* 2003).

Biomass energy is another form of captured solar energy, and it has the advantage of solar energy being stored in the biomass for concentrated processing and delivery. Shinnar and Cintro (2006) have proposed a roadmap to switch to non-fossil fuels over the next 30 to 50 years that rely on proven and available technologies that include solar, geothermal, wind, hydro and nuclear technologies. Roughly 15% of the land area in the US is currently used for cultivation, and most of that for food (*Grant* 2003). The energy value of these crops is estimated to be 2.6 TW of energy, which clearly is not sufficient to meet existing energy needs alone (and what would we eat?). However, to produce sufficient hydrogen to meet our transportation infrastructure with crops we would need 0.4 TW to make hydrogen via water electrolysis. This is equivalent to an increase in cultivation to 18% of the land (*Grant* 2003).

Costs to replace 70% of the fossil fuels (and most coal sources) would cost $170 to $200 billion per year over the next 30 years (*Shinnar and Cintro* 2006). While such economic figures are indeed challenging, they are not insurmountable. Given this long time frame, it is also likely that new technologies could emerge that could change the economic assessment. Thus, our best solution for both energy and climate appears to be heavy investment in renewable energy resources, in terms of both research and development.

1.3 Bioelectricity generation using a microbial fuel cell—the process of electrogenesis

Microbial fuel cell (MFC) technologies represent the newest approach for generating electricity—bioelectricity generation from biomass using bacteria. While the first observation of electrical current generated by bacteria is generally credited to Potter in 1911 (*Potter* 1911), very few practical advances were achieved in this field even 55 years later (*Lewis* 1966). In the early 1990s, fuel cells became of more interest and work on MFCs began to increase (*Allen and Bennetto* 1993). However, experiments that were conducted required the use of chemical mediators, or electron shuttles, which could carry electrons from inside the cell to exogenous electrodes (see Chapter 2). The breakthrough in MFCs occurred in 1999 when it was recognized that mediators did not need to be added (*Kim et al.* 1999c; *Kim et al.* 1999d).

In an MFC, microorganisms degrade (oxidize) organic matter, producing electrons that travel through a series of respiratory enzymes in the cell and make energy for the cell in the form of ATP. The electrons are then released to a terminal electron acceptor (TEA) which accepts the electrons and becomes reduced. For example, oxygen can be reduced to water through a catalyzed reaction of the electrons with protons. Many TEAs such as oxygen, nitrate, sulfate, and others readily diffuse into the cell where they accept

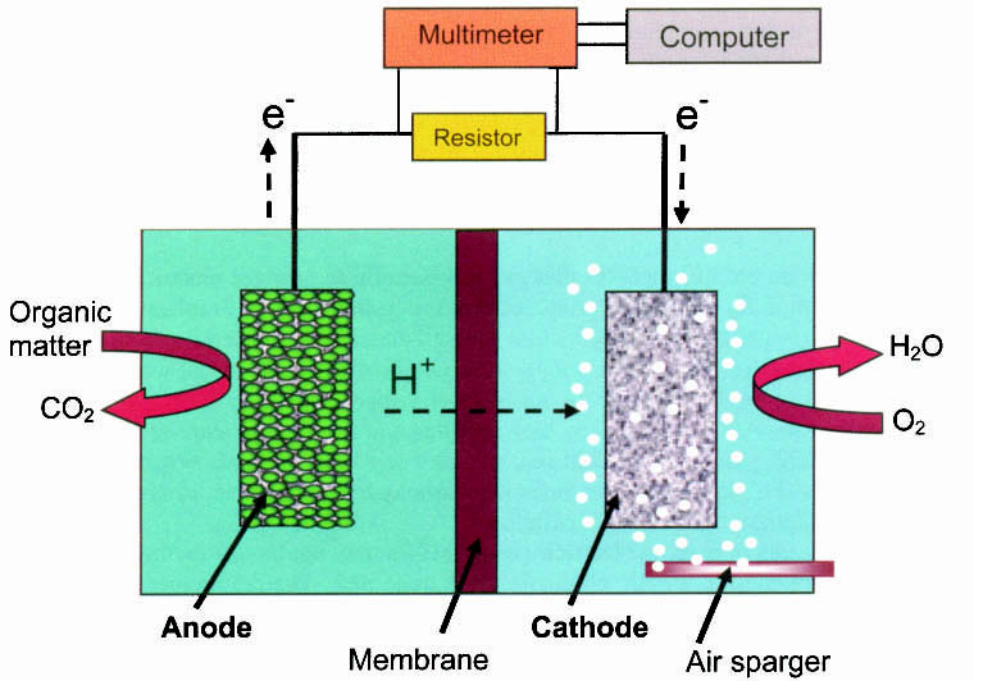

Fig. 1.3 Schematic of the basic components of a microbial fuel cell (not to scale). The anode and cathode chambers are separated by a membrane. The bacteria grow on the anode, oxidizing organic matter and releasing electrons to the anode and protons to the solution. The cathode is sparged with air to provide dissolved oxygen for the reactions of electrons, protons and oxygen at the cathode, with a wire (and load) completing the circuit and producing power. The system is shown with a resistor used as the load for the power being generated, with the current determined based on measuring the voltage drop across the resistor using a multimeter hooked up to a data acquisition system.

electrons forming products that can diffuse out of the cell. However, we now know that some bacteria can transfer electrons exogeneously (*i.e.,* outside the cell) to a TEA such as a metal oxide like iron oxide. It is these bacteria that can exogenously transfer electrons, called *exoelectrogens*, that can be used to produce power in an MFC. The nomenclature used for categorizing process, microorganisms, and reactors for methane generation is: methanogenesis, methanogens, and anaerobic digesters. Similarly, we classify this method of electron-generating process as *electrogenesis*, with the bacteria *exoelectrogens* and the reactor a *microbial fuel cell (MFC)*.

A schematic of an MFC system is shown in Fig. 1.3. Oxygen in the anode chamber will inhibit electricity generation, so the system must be designed to keep the bacteria separated from oxygen (the catholyte in this example). This separation of the bacteria from oxygen can be achieved by placing a membrane that allows charge transfer between the electrodes, forming two separate chambers: the anode chamber, where the bacteria grow; and the cathode chamber, where the electrons react with the catholyte. The cathode

is sparged with air to provide dissolved oxygen for the reaction. The two electrodes are connected by a wire containing a load (*i.e.,* the device being powered), but in the laboratory a resistor is used as the load. In principle, the membrane is permeable to protons that are produced at the anode, so that they can migrate to the cathode where they can combine with electrons transferred via the wire and oxygen, forming water. The current produced by an MFC is typically calculated in the laboratory by monitoring the voltage drop across the resistor using either (a) a voltmeter (intermittent sampling) or (b) a multimeter or potentiostat hooked up to a computer for essentially continuous data acquisition.

The development of processes that can use bacteria to produce electricity represents a fantastic method for bioenergy production as the bacteria are self-replicating, and thus the catalysts for organic matter oxidation are self-sustaining. Bacterial reactions can be carried out over several different temperature ranges depending on the tolerance of the bacteria, ranging from moderate or room-level temperatures (15–35°C) to both high temperatures (50–60°C) tolerated by thermophiles and low temperatures (<15°C) where psychrophiles can grow. As we shall see, virtually any biodegradable organic matter can be used in an MFC, including volatile acids, carbohydrates, proteins, alcohols, and even relatively recalcitrant materials like cellulose.

While the idea of making electricity using MFCs may not be new in theory, certainly as a practical method of energy production it is quite new. The requirements for making MFCs economically viable as a method of energy production are demanding. The cost of oil currently remains low, and there are many different alternative methods of energy production that have reached a high level of development making them competitive for energy production. MFCs are so new that relatively little effort has been put into practical architectures using affordable materials. As highlighted in this book, however, that is already changing and many new approaches for MFC design are yielding promising results. When a new technology is developed, the fastest way to bring it to the market is to apply it in an area most likely to yield the greatest profit. As the technology further develops, it can then reach new markets. Computer hard drives needed many years of development, for example, before they could be small enough to be portable as music players. Similarly, MFCs should be developed for application in the area that will likely produce the greatest profit. For many reasons described below, it appears that the first and most useful widespread application of MFCs will be as a method of energy recovery to make the water infrastructure sustainable.

1.4 MFCs and energy sustainability of the water infrastructure

Over two billion people on the planet lack adequate sanitation, and one billion do not have sufficient access to potable water. Energy demands for conventional water and wastewater processes are a large part of the problem. In the US, we use approximately 4-5% of our electricity production for the water infrastructure, which includes water treatment and distribution, and wastewater collection and treatment. Approximately 1.5% of our electricity goes to wastewater treatment alone. The costs for maintaining the infrastructure are significant, with an annual cost for wastewater treatment of $25 billion. It is expected that over the next twenty years an additional $45 billion will need to be expended to maintain and improve this infrastructure (*WIN* 2001).

Wastewaters contain energy, in the form of biodegradable organic matter, that we expend energy to remove rather than trying to recover it. At a conventional wastewater

treatment plant in Toronto, Canada, it was estimated that there was 9.3 times as much energy in the wastewater than was used to treat the wastewater (*Shizas and Bagley* 2004). Domestic, animal and food processing wastewaters are estimated to contain a total of 17 GW. This is about the same amount of energy that is currently used for the whole water infrastructure in the US (*Logan* 2004). Thus, if we could recover this energy we could make the water infrastructure self sufficient. Such an achievement would be a huge benefit to the health and well being of the US in the coming years of energy uncertainty. More importantly, such treatment processes could improve the quality of human life globally, as well as contribute to the reduction of the spread of waterborne disease through untreated sewage. Anaerobic digestion processes, based on methane generation can be an important part of energy generation from waste materials. However, they require relatively elevated temperatures (36°C) and long detention times, making them suitable only for high-strength wastewaters.

1.5 MFC technologies for wastewater treatment

Microbial fuel cell (MFC) technologies are a promising and yet completely different approach to wastewater treatment as the treatment process can become a method of capturing energy in the form of electricity or hydrogen gas, rather than a drain on electrical energy. In the late 1990s, Kim and coworkers demonstrated that bacteria could be used in a biofuel cell as a method of determining the concentration of lactate in water (*Kim et al.* 1999d), and then that electricity generation in an MFC could be sustained by starch using an industrial wastewater (*Kim et al.* 1999c). However, the power production was low and it was not clear whether the technology would have much impact on reducing wastewater strength. In 2004, this changed and the link between electricity using MFCs and wastewater treatment was clearly forged when it was demonstrated that domestic wastewater could be treated to practical levels while simultaneously generating electricity (*Liu et al.* 2004). The amount of electricity generated in this study, while low (26 mW/m^2), was considerably higher (several orders of magnitude) than had previously been obtained using wastewater. Research led by Reimers (2001) a few years earlier had demonstrated that organic and inorganic matter in marine sediments could be used in a novel type of MFC, making it apparent that a wide variety of substrates, materials, and system architectures could be used to capture electricity from organic matter with bacteria. Still, power levels in all these systems were relatively low. The final development that sparked the current interest in MFCs was provided by Rabaey *et al.* (2003) when they demonstrated power densities two orders of magnitude greater was possible in an MFC using glucose, again without the need for exogenous chemical mediators.

Following these demonstrations, the race was on to develop practical applications of MFCs, with the first goal being development of a scaleable technology for the treatment of domestic, industrial, and other types of wastewaters (*Logan et al.* 2006). While the energy that could be captured from wastewater is not enough to power a city, it is large enough to run a treatment plant. With advances, capturing this power could achieve energy sustainability of the water infrastructure. As an example of the power that can be derived from wastewater, consider the example that follows for energy recovery for a modest-sized town.