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Using Bioelectrochemical Systems for Sustainable Desalination

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USING BIOELECTROCHEMICAL SYSTEMS FOR SUSTAINABLE DESALINATION

By Bo Zhang

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ABSTRACT

USING BIOELECTROCHEMICAL SYSTEMS FOR SUSTAINABLE DESALINATION

By

Bo Zhang

At University of Wisconsin, Milwaukee, 2013

Under the supervision of Dr. Zhen He

Desalination of seawater or brackish water holds the potential to solve the freshwater shortage that is threatening nearly half of the world population. Current desalination technologies are energy intensive, which makes the desalinated water prohibitively expensive. In this study, investigations have been made to use renewable energy sources from organic waste to power the desalination process. Since desalination is driven by renewable energy, such desalination systems are more sustainable than currently widely employed commercial technologies. Efforts have been made to study how to operate BES driven desalination process such that the energy consumption will be minimized. Forward osmosis technology is also incorporated into BES system for desalination and water reclamation. Two types of FO-BES combined systems are studied here. In this first type, the FO was used as separator in Microbial Desalination Cell (MDC) to achieve the goals of desalination and water reclamation in a single BES. In the second type of system, the MDC was connected with an Osmotic Microbial Fuel Cell (OsMFC). The water reclamation is achieved in OsMFC while the task of desalination is left for MDC. A cost effective cathode catalyst is also prepared in order to lower the capital cost of BES for full scale...
application. The catalyst is based on activated carbon, which is relatively cheaper to noble metal catalysts, and can be prepared by using simple methods. The activated carbon based catalyst showed high catalytic activity toward oxygen reduction reaction and achieved higher current density than Pt based catalyst.
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Chapter 1 Introduction

1.1 Background of Desalination
Limited freshwater availability is becoming a global issue. A recent study shows that one billion of global population will live in areas stricken by freshwater shortage by 2050. This issue need to be addressed before it becomes a global crisis.

Apart from natural hydrologic cycle of freshwater, desalination of seawater and brackish water is the only means of increase water supply to areas stricken by water shortage. Generally speaking, the total dissolved solids concentration (TDS) of seawater is above 35 g/L, whereas the TDS of brackish water is typically around 5 g/L. On the other hand, the maximum allowable TDS for drinking water and agricultural application water is much lower. For instance, the drinking water TDS should be maintained below 0.5 g/L. When water is applied to agricultural crops, other criteria, such as boron concentration has to be met in addition to total dissolved solids concentration.

It is obvious that either seawater or brackish water has to be properly desalinated before they could be applied as replenishment to freshwater. Currently, the most widely used desalination technologies are reverse osmosis (RO) and electrodialysis (ED).

In RO, a piece of semi-permeable membrane is used to separate water and dissolved salts. The pore size of RO membranes is typically in the range of 1 nm and could be as low as 0.1 nm. With such a pore size, most of the dissolved salts will be rejected while water molecules could be
pushed through the membrane under high pressures. The pressure required to desalinate seawater and brackish water are in the ranges of 600 – 1200 psi and 30 – 250 psi, respectively.

ED is another commonly used desalination technology. The desalination process in ED depends on ion exchange membranes. In ED, multiple pairs of cation exchange membrane (CEM) and anion exchange membrane (AEM) are inserted between anode chamber and cathode chamber. When applying a potential (normally this potential should be high enough to trigger hydrogen and oxygen evolution reaction in cathode and anode respectively), water is oxidized to oxygen in anode and reduced to hydrogen in cathode. During this reaction, electrons are released to anode and travel to cathode. In order to maintain electro-neutrality, for each electron that is released, one pair of anion and cation will be desalinated in each pair of ion exchange membrane. It should be noted that as the number of ion exchange membrane pair increase, the desalination efficiency for one electron is higher. However, as the number of ion exchange membrane pair increase, the internal resistance of ED cell will also increase, thus a typical ED unit will control the number of ion exchange membrane pair to 50 to 100. Although RO and ED are efficient desalination technology, high energy cost associated with these technologies need to be reduced. For example, the most efficient RO process requires 3 – 7 kWh of energy to produce 1m³ of freshwater from seawater².
The high energy cost hampers the proliferation of desalination plant and reduces the availability of desalinated water to a greater population. In order to offset the high energy demand of desalination process, researchers and engineers eye on renewable energy to partially or completely drive the desalination process. 
Among various renewable energy sources, Bioelectrochemical systems (BES) are a family of systems that either generates electricity or value-added products. Microbial Fuel Cell (MFC) is the most simple and fundamental BES. In MFC, electrochemically active bacteria grown on anode oxidize organic matters present in anolyte. During the oxidation, these bacteria will release electrons to anode, and hydrogen ions into electrolyte. The electrons will flow from anode, through an external circuit, to cathode, where it is combined with a terminal electron acceptor (typical electron acceptor is oxygen in air).

Fig. 1.3 A schematic diagram of Microbial Fuel Cell (Image from: 6)

Typical MFC uses a piece of ion exchange membrane as a separator between anode chamber and cathode chamber 6. However, if we insert one pair (or multiple pairs) of ion exchange membrane between anode and cathode, MFC can be converted to a device called Microbial Desalination Cell (MDC), which has the capability of desalinating salt water 7-9.
The electrode reactions in MDC are similar to those in MFC. In brief, bacteria grown on anode oxidize organic matters, releases electrons to anode and hydrogen ions to cathode. The electrons collected by anode travel to cathode where it is combined with a terminal electron acceptor. However, since hydrogen ions (H$^+$) are discharged into anolyte during anodic reactions, the electro-neutrality of anolyte is broken, and this neutrality has to be restored through ion movement. In MDC, negative ions in middle chamber (such as Cl$^-$) will migrate through anion exchange membrane to anolyte. Migration of anions will restore the electro-neutrality of anolyte. Similarly, in cathode reaction, when oxygen is used as terminal electron acceptor, OH$^-$ will be discharged into catholyte; the cations in middle chamber will migrate through cation exchange.
membranes to maintain electro-neutrality in catholyte. In summary, the current flow through the cell is the main driving force of desalination. For one electron transferred, there will be one hydrogen ion being discharged to anolyte and one hydroxide ion released to catholyte. And to maintain electro-neutrality in anolyte and catholyte, one anion and one cation will be removed from salt chamber.

Various modifications has been made to the MDC first devised by Cao et al. Jacobson et al. used a tubular MDC to increase desalination efficiency, Chen et al and Kim et al tried to increase MDC desalination performance by inserting multiple pairs of ion exchange membranes between anode and cathode in a fashion similar to ED. Other modifications include microbial electrodialysis desalination cell (MEDC) and microbial reverse electrodialysis cell (MRC). In MEDC, external voltage is applied to anode and cathode of MDC to achieve simultaneous desalination and hydrogen production. In MRC, instead of desalination, salt water and fresh water are filled to the chambers between anode and cathode, the voltage existed between salt water and fresh water is captured and used to drive hydrogen producing reaction.

1.2 Objectives of the research
The objectives of this study are to investigate how to use BES systems to achieve the goal of desalination and wastewater treatment. We want to develop the prototypes of new desalination technologies that use renewable energy sources from wastewater to power desalination alone, or, to offset some of the energy demand of downstream processes. In addition to that, it is beneficial to reclaim some water from wastewater using membrane technologies. Various factors that affect
the performance of BES are studied. The focus of the current research is placed on desalination, however, wastewater treatment performance is also considered.

1.3 Outline of the thesis
The thesis consists of seven chapters. In chapter one, a brief introduction to the background of desalination and current desalination technology is given. In chapter 2, the different BES systems and forward osmosis technology are reviewed. In chapter 3, experimental proof of BES could facilitate sustainable desalination is given and different operation modes of BES are studied to examine the effect on energy saving. In chapter 4, the forward osmosis process is incorporated into BES to achieve the goal of desalination and water reclamation simultaneously. In chapter 5, a combination of two BES is studied to address the limitation of using forward osmosis in desalination. In chapter 6, a cost effective catalyst is synthesized using readily available materials and simple processing method. The goal of this catalyst is to lower the cost of BES so that this technology could be bringing into full scale application. In chapter 7, conclusions are drawn and suggestions for future works are given.
Chapter 2 Literature Review

2.1 Bioelectrochemical System (BES)

BES refers to systems that rely on electrochemically active bacteria to facilitate the redox reactions. BES is one of the most versatile systems that is being studied in the field of environmental engineering. Depends on the purpose of the system, the electrochemically active bacteria could develop either on anode or cathode. When bacteria develop on anode, they could oxidize the organic matters that present in anolyte and release the electrons to anode. The electrons will travel through an external circuit and combine with the electron acceptors on cathode. In this sense, an MFC is formed. On the other hand, if the electrochemically active bacteria are employed on cathode. They could act as catalyst to facilitate the oxygen reduction reaction\(^{15}\), hydrogen evolution reaction\(^{16}\), formation of methane\(^{17}\) and biosynthesis\(^{18}\).

There are some disputes on how the electrons are transferred from the bacteria to the electrode. The two competing theories are electron-hopping\(^{19}\) and nanowires\(^{20}\). Both approaches have been reported by different groups as possible ways of electron transfer. In electron-hopping approach, the redox active mediators, such as flavin and riboflavin, act as vehicles. The electrons jump from the cell to mediator and from mediator to another mediator until it reaches the surface of the electrode. However, although electron hopping is a well-established model of extra-cellular electron transfer, it has been observed only in short distances (typically in several nanometers). The distance of the electrochemically active bacteria to the electrode is in the order of \(\mu m\) thus some researchers have questioned its validity in BES. On the other hand, the nanowire theory speculates that the electrons are transferred from bacteria to electrode via the
conductive pili that the bacteria synthesized. The pili synthesized are typically several nanometers in diameter and could be as long as several μm. The one end of the pili attached to the electrochemically active bacteria and the other end either attaches to the electrode or to other pili, in this way, these pili will form a grid through which the electrons could transfer. The mechanism of extracellular electron transfer remains an active research topic in BES\textsuperscript{21-22}.

\section*{2.2 Microbial Fuel Cell (MFC)}

MFC is first proposed as an alternative wastewater treatment technology to activated sludges\textsuperscript{23}. The benefit of MFC is two folded. First of all, MFC does not need aeration, which could account for more than 50\% of the operating cost of current wastewater treatment plant. On the other hand, MFC is an anaerobic process, thus it produces less sludge that need to be properly disposed of. However, the first MFC use wastewater to produce electricity was first reported using a single chamber MFC\textsuperscript{24}. After that, numerous reports have been published using various feed solutions, such as manure, brewery wastewater and organic matters in the sediment.

The configurations of MFC have also evolved into ones that are more realistic for full scale application. Early works of MFC use H shaped reactors with carbon cloth or carbon fiber as the anode electrode. The H shape reactors use a salt bridge to connect the anode and cathode, in addition to that, the distances of the two electrodes is usually in the order of 10 cm. The salt bridge and the large distance between two electrode results in high internal resistances, which lower the power output of MFC and current generation. It is recognized among researchers that
better configurations are needed if MFC to be applied as the next generation wastewater
treatment technology.

The commonly used MFC configurations in lab and pilot scale studies include single chamber
MFC, tubular MFC, flat plate MFC and stacked MFC. In single chamber MFC, the separators
are eliminated and the anode electrode is placed in close distance from the cathode electrode. In
this way, the internal resistance is reduced to the lowest extent. Another advantage of single
chamber MFC is the elimination of catholyte. In single chamber MFC, the anode chamber and
cathode chamber shares the same electrolyte, which typically is wastewater. By eliminating the
need of catholyte, the operation cost of MFC is reduced.

Another commonly used MFC is tubular MFC. In a tubular MFC, a tube shaped reactor is
formed either by plastics or membranes. The anode electrode and cathode electrode are separated
by the tube and are also in close distance. The advantage of tubular MFC is that it has low
internal resistance and high membrane area for ion exchange when the ion exchange membrane
is used to form the tube. These two factors contribute the higher power output of tubular MFC.

Since the voltage output of single MFC is limited by the thermodynamic limitations on anode
and cathode (1.2 V, if use oxygen as the electron acceptor), a natural thought to increase the
voltage of MFC is to used several MFC in serial connection. In this way, a stack MFC is formed.
Stack MFC consists of several flat plate MFCs, each flat plate MFC has its own anode and
cathode, the anode and cathode of different flat plate MFCs are connected in serial mode to increase the output voltage of MFC \(^{26}\). A recent lab study shows that stack MFC could supply enough voltage and power to drive the pumps for lab scale MFC operation \(^{27}\).

The electron acceptors used in MFC include oxygen (air) \(^{23}\), potassium ferricyanide \(^{28}\) and manganese \(^{29}\). Among them, oxygen is deemed as the electron acceptor that is most suitable for large scale MFC application. First, the oxygen reduction reaction has a high redox potential comparing to other cathode reactions. Second, the oxygen is readily available from the air and does not need to be purchased or replaced like other chemicals.

2.3 Microbial Desalination Cell (MDC)

MDC is a derivation of MFC \(^{7}\). It combines the BES system with ED for desalination in a sense that the electrochemically active bacteria are employed on the anode to drive redox reactions and electron flows, and pairs of ion exchange membranes in between the two electrodes to facilitate the desalination. A schematic diagram of MDC is shown in Fig. 1.4.

The bioelectricity generation and desalination are linked by the principle that electro-neutrality has to be maintained in the solution. When anode bacteria oxidize organic matters and release electrons to the anode, one hydrogen ion is discharged into the anolyte, thus to maintain electro-neutrality in anolyte, a negative ion has to move into the anolyte from adjacent salt solution chamber. Likewise, the cathode chamber will be deficient in positively charged ions when the
electron from anode is combined with hydrogen ion in catholyte. In order to maintain electro-
neutrality in catholyte, a positive ion has to move across the ion exchange membrane from the
chamber next to cathode. The ion movements will replicate in each chambers and due to the
selectivity of ion exchange membranes, some chambers will have desalinated water (dilute)
while others have solutions with higher salinity (concentrate). The dilute then will be collected as
desalinated water as a replenishment to fresh water supply. As mentioned above, there is no
external power needed to drive the MDC for desalination, the sole energy source for desalination
comes from the organic matters in anolyte (wastewater). This feature is particularly attractive
since energy cost could be eliminated or reduced for desalination.\textsuperscript{8}

Since the desalination in MDC is driven by electrochemically active bacteria, the desalination
rate is very low comparing to RO or ED processes. Whereas in RO and ED the desalination will
take several hours, a study showed that desalination of 35 g/L of NaCl solution could take as
long as 4 days.\textsuperscript{9} Thus, the research effort of MDC has been focused on improving desalination
efficiencies.

The desalination efficiency of MDC could be increased by several means. First of all, it is
helpful to increase the membrane area so that the internal resistance could be lowered.\textsuperscript{9} Second,
stacked salt chambers has been proposed to duplicate the effect of each electron transferred in a
similar fashion to ED.\textsuperscript{10} With better membrane configuration, Kim et al.\textsuperscript{11} improve the number
of salt chamber pairs from 1.5 to 5 to allow better desalination efficiency. Another method of
making MDC more economically viable is to apply an external voltage across the anode and
athode to produce hydrogen in cathode chamber. In addition to hydrogen production, the applied voltage could alleviate the polarization in electrodes thus allows the MDC to reach higher current. The produced hydrogen could provide more energy than that consumed by the power supply and the excess hydrogen could be sold as an renewable energy source.

2.4 Forward Osmosis
During the study of desalination using MDC in our group, we observed that there was water flux from anode chamber to the salt chamber. This water flux achieves two goals, one is dilution of salt water, and the other is water reclamation from wastewater. Bearing this in mind, an effort has been made to seek water flux from anode to cathode with higher flux and better selectivity towards water molecules. This has been achieved by using a forward osmosis membrane as separator between salt chamber and anode chamber.

Forward osmosis is a process based on semi-permeable membranes and utilizes the differences of water chemical potential in two different solutions. The forward osmosis membrane consists of a selective layer and a supporting layer. The role of supporting layer is to provide the membrane with mechanic strength to withstand the high pressures during operation. The selective layer is formed by polymers and has pore sizes below 1 nm. The small holes allow only the passage of water molecules and will reject most of the ions.

The driving force of water molecules movement is the water chemical potential difference. The concentrate solution and dilute solution is separated by forward osmosis membrane. Since the
water molecules in dilute solution have higher water chemical potential, it tends to migrate through the forward osmosis membrane to the more concentrate solution. It has been estimated that the driving force in this process could be equivalent to 270 m in hydraulic head when using river water as the dilute solution and seawater as the concentrate solution 32.

Previously, the research of forward osmosis has been focused on using physical chemical processes to achieve desalination. In such a system, a solution with high osmotic pressure is used as the concentrate solution to draw water from seawater, the solution later will be treated to remove and reuse the solutes while the water will be used as desalinated water 33.

Another way of utilizing the salinity gradient for renewable energy production is call pressure retarded osmosis (PRO). In PRO system, a pressure is applied at the concentrate solution side. Since water molecules move through the forward osmosis membrane into the concentrate solution, the pressure of concentrate solution will increase until it reaches a level of overcome the applied pressure. Upon overcoming the applied pressure, the water flux could turn the turbine of a power generator and convert the salinity gradient energy to electrical energy 34. The research of PRO process has been focused on developing better forward osmosis membranes that has lower mass transfer resistance 35, better selectivity to water molecules and the ability to withstand higher applied pressures 36.
Chapter 3 Energy production, use and saving in a bioelectrochemical desalination system

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Abstract

Microbial Desalination Cells (MDCs) has been suggested as a pretreatment technology to save energy in downstream processes. However, to our best knowledge, no research has been done to systematically investigate in which operation mode MDCs saves the most amount of energy. In this research, we operated upflow microbial desalination cells (UMDCs) in eight operation modes: serial/parallel connection in high power mode, serial/parallel connection in high current mode, serial/parallel connection charging battery mode, and, serial/parallel connection charging capacitor mode, to quantitatively investigate energy saving by MDC technology. Both serial and parallel connections of UMDCs achieved comparable performance in desalination and energy production. Direct charging in a serial connection transferred 86.6% of the energy from the UMDC system to a rechargeable battery, and 41.8% of the energy to an ultracapacitor, suggesting that ultracapacitors that are designed for quick charging may not be suitable for energy extraction from bioelectrochemical systems. About half of the stored energy in the rechargeable battery or ultracapacitor was lost when powering downstream desalination process. The parallel connection aided by a DC-DC converter did not successfully charge either the rechargeable battery or the ultracapacitor. Overall, serial connected UMDCs operated in charging battery mode is more energy efficient than other modes in our study. However, if
energy storage and reuse efficiency could be enhanced to above 52%, serial connected UMDCs operated in high power mode is more energy efficient.

3.1. Introduction

Desalinating brackish water offers an opportunity to significantly increase the freshwater supply for drinking and other purposes in regions where access to freshwater is limited; however, the intensive consumption of energy by current desalination technologies is a major drawback, resulting in high operating costs and water prices. The use of renewable energies, such as solar and wind, to drive desalination helps to build a sustainable desalination approach in terms of energy resources and environmental effects, but the high costs and uncertainties associated with utilizing these renewable energies remains a significant challenge. As a result, the shortage of freshwater resources and high cost of current desalination processes have created a demand for new desalination technologies with both environmental and economic benefits.

Recent advancements in bioelectrochemical systems introduced the concept of using the microbial desalination cell (MDC) as an alternative desalination method, which has received a great attention. Derived from microbial fuel cells (MFCs), MDCs use electric potential generated from the microbial metabolism of organic compounds to drive desalination, similar to electrodialysis (ED). The advantages of an MDC include less external energy for the desalination process and simultaneous wastewater treatment, and researchers have further developed the MDC concept in several ways. For example, a ferricyanide cathode was replaced by an air cathode with a reduced amount of anolyte required for desalination. Continuously-operated MDCs were developed with upflow configuration at different scales and salt removal could be
achieved from either NaCl solution or seawater. Desalination efficiency improved with multiple membrane pairs, mimicking EDs. When oxygen is removed from the cathode and an external potential is applied to MDCs, hydrogen gas can be produced during desalination.

Although MDCs are promising as a low-energy desalination method, their limitations must be understood to find a suitable application niche. It was believed that the primary function of MDCs is wastewater treatment, and desalination is a “bonus” effect that takes advantage of bioenergy production during the treatment process. Research demonstrates that MDCs can generally remove salts well at the expense of a lengthy retention time of several days, which will requires a large reactor volume as compensation, thereby increasing capital investment. The low desalination efficiency (in terms of retention time) has two implications for MDC application: First, MDCs may be more appropriate as pre-desalination units in connection with conventional desalination process downstream. Partial reduction of salinity could result in significant energy savings in downstream desalination, and this concept has been proposed and theoretically analyzed, but there has not been experimental verification. Second, MDCs may be more suitable for desalinating brackish water instead of seawater. A lower salinity in feeding water will lead to a shorter period of desalination time in MDCs, compensating for slow salt removal.

Another issue regarding MDC operation raised by our previous studies is the production of electric energy vs. electric current. MDCs can produce electricity like that in MFCs. Contradictory results are obtained when evaluating electricity generation and desalination: high-
current generation can remove more salt, but little power is harvested; high-power production can produce more electric energy that may offset energy consumption by downstream desalination, but desalination efficiency is low in MDCs. Although our previous study concluded that high-power operation could be beneficial because of energy production, the analysis was based on the assumption that 100% of energy produced in MDCs could be used by the downstream desalination process, and actual operation will expect a large loss of energy during transfer, storage, and use. Therefore, it is necessary to examine this phenomenon experimentally.

In this study, the previously developed upflow MDCs (UMDCs) were used. A lab-scale Electrodialysis (ED) cell is used as a vehicle to mimic downstream desalination process in our experiments. Experiments were conducted to perform three tasks: 1) investigate the energy benefits of using an UMDC as pre-desalination unit; 2) examine energy production and desalination performance of the UMDCs operation different operational modes; and 3) study the possibility of in situ usage of renewable bioenergy produced by UMDCs to power downstream desalination process.

3.2. Materials and Methods

3.2.1 UMDC Setup and Operation.
UMDCs used in this study are built and operated similar to the ones employed in our previous research [10]. Briefly, the UMDCs are tubular reactors made of ion exchange membranes (Membrane International, NJ, USA). Carbon brush and carbon cloth (with Pt as catalysts) were
used as the anode and the cathode electrodes, respectively. The liquid volume is 1.9 L for the anode compartment and 0.85 L for the salt compartment. More details of UMDC construction and schematics can be found in our previous publication \(^{46}\). A single UMDC or three UMDCs were employed in this study for different purposes. When three UMDCs were operated, they were electrically connected either in series or in parallel.

The UMDCs were operated under a room temperature of ~ 20 °C. UMDCs were connected to a 0.1 ohm resistor when operated in high current mode. When operated in high power mode, the load of circuit was set equal to internal resistance of the UMDCs obtained from polarization test.

The anolyte contained (per L of tap water): sodium acetate, 2 g; NH\(_4\)Cl, 0.15 g; NaCl, 0.5 g; MgSO\(_4\), 0.015 g; CaCl\(_2\), 0.02 g; KH\(_2\)PO\(_4\), 0.53 g; K\(_2\)HPO\(_4\), 1.07 g; yeast extract, 0.1 g; and trace element, 1 mL \(^{51}\). The anolyte was fed at 4 mL/min, resulting in a hydraulic retention time (HRT) of ~ 8 hours, and was recirculated at 150 mL/min. The initial anode inocula were a mixture of aerobic and anaerobic sludge from South Shore Wastewater Treatment Plant (Milwaukee, WI). Artificial brackish water was prepared by dissolving NaCl in tap water (6 g/L). For single-UMDC operation, brackish water was continuously fed into the salt compartment of the UMDC in an upflow mode and the flowrate was adjusted to obtain the desired HRTs. For three-UMDC system operation, brackish water was fed as sequence batch in which brackish water was completely replaced after 18-h desalination. Continuous feeding of brackish water was also examined with the three-UMDC system. The catholyte was the acidified water (adjusted with sulfuric acid) at a pH of 2.5 and was used to rinse the cathode electrode from the top to the bottom at a flowrate of 4 mL/min. The use of the acidified water benefited electricity generation.
and had a much lower cost (3%) compared to the phosphate buffer solution that is commonly used in bioelectrochemical studies. The “HRT” in the results and discussion refers to the retention time of brackish water, unless stated elsewhere.

3.2.2 Electrodialysis Operation
A commercially available lab-scale electrodialysis (ED) (64002, PCCell GmbH, Heusweiler, Germany) was operated at room temperature in this study as a vehicle to mimic downstream desalination unit operations. The ED contains 10 cell pairs, each of which is assembled with standard ion exchange membranes (PC-SK and PC-SA) and spacer. The active surface area of each membrane is 64 cm$^2$. The anode electrode is Pt/Ir-MMO-coated Ti-stretched metal, and the cathode electrode is stainless steel. Electrolytes for both the anode and the cathode are Na$_2$SO$_4$ (100 mM), and were recalculated at a rate of 100 mL/min. The effluent from the UMDC operation, as the feeding water to the ED, was equally divided into two parts, which were then pumped into the ED as concentrated and diluted solutions (recirculated at 100 mL/min), respectively; therefore, the water recovery rate was 50%. A power supply (3465A, Circuit Specialists Inc., Mesa, AZ, USA) provided voltage for the ED operation (5 V for the effluent from the single-UMDC operation and 10 V for the effluent from the three-UMDC system), unless a rechargeable battery or an ultracapacitor was used.
Fig. 3.1. Connections of electric circuits during charging and discharging: (A) direct charging with serial connection of the UMDCs; (B) indirect charging with parallel connection of the UMDCs; and (C) discharging with the aid of a DC-DC converter to power the ED.

### 3.2.3 Charging and Discharging

Two approaches were adopted for extracting electric energy from the UMDCs. The first approach was direct charging. When the three UMDCs were connected in series, the rechargeable battery or ultracapacitor was directly connected to the UMDC circuit for direct charging to a voltage of 1.2 V (rechargeable battery) or 2.7 V (ultracapacitor) (Fig. 3.1A). When the three UMDCs were connected in parallel, a DC-DC converter was applied to the electric circuit to increase the cell voltage to 3.3 V for charging (Fig. 3.1B). The DC-DC converter (TPS61200, Texas Instruments, Dallas, TX, USA) was successfully applied in our previous study of sediment MFC and proved effective in voltage elevation. The ultracapacitor (Maxwell Technology, Inc., San Diego, CA, USA) has a capacitance of 350 F and voltage rating of 2.7 V. The energy stored in an ultracapacitor was calculated according to our previous publication.

The rechargeable battery has a capacity of 1000 mAh (DC2400 NiMH rechargeable AAA battery, Duracell, Bethel, CT, USA). Before charging, the rechargeable battery or ultracapacitor was discharged through the ED until a condition that current in ED became zero, indicating that the rechargeable battery or ultracapacitor did not have enough energy to activate the ED process. The discharging of a rechargeable battery or an ultracapacitor to the ED was conducted with the
aid of the DC-DC converter (Fig. 3.1C).

3.2.4 Measurement and Analysis
The cell voltage was recorded every 60 seconds by a digital multimeter (2700, Keithley Instruments, Inc., Cleveland, OH, USA). The pH was measured using a benchtop pH meter (Oakton Instruments, Vernon Hills, IL, USA). The conductivity was measured by a benchtop conductivity meter (Mettler-Toledo, Columbus, OH, USA). The polarization curve was performed by a potentiostat (Reference 600, Gamry Instruments, Warminster, PA, USA) at a scan rate of 0.2 mV/s. Energy consumption by the ED was calculated by integrating power consumption with time. The charging efficiency was defined as the ratio between energy delivered into the energy-storage units and theoretic energy produced in the UMDC system (computed from high-power operation). The discharging efficiency was the ratio between energy released to the ED and energy charged into the energy-storage units. The overall efficiency, or energy recovery efficiency, was the ratio between energy released to the ED and energy produced in the UMDC system. When a rechargeable battery or an ultracapacitor was used to power the ED, the (additional) ED energy requirement was calculated by the difference between the energy release from those energy-storage units to the ED when desalinating one liter of the UMDC effluent and the energy consumption of the ED (operated by a power supply) when desalinating one liter of the same effluent.
3.3. Results

3.3.1 Single UMDC as Pre-desalination before an ED
A single UMDC was operated and its saline effluent was transferred to an ED for further desalination. The results clearly demonstrated the benefit of using MDCs as pre-desalination units (Fig. 3.2). At an HRT of 13.75 h and an external resistance of 0.1 Ω, the UMDC reduced the conductivity of brackish water from 10.89 to 6.28 mS/cm. When this water was further desalinated by the ED at an applied voltage of 5 V, it consumed 1578 ± 16 J and took 90 min to decrease the conductivity to 1.08 mS/cm. For comparison, the same amount of original brackish water without the UMDC pre-desalination required 2885 ± 25 J and 120 min to reach 1.19 mS/cm in the ED — a saving of 45.3 % in energy consumption and 25.0 % in desalination time.

![Graph showing current and conductivity over time](image)

Fig. 3.2. Comparison of current generation and solution conductivity in the ED between desalinating the original brackish water (solid line and dark circle) and the UMDC effluent (dashed line and white circle).

The performance of the UMDC directly affected the energy consumption by the ED. The UMDC was operated at three different HRTs, 18, 13.75, and 6 h (at an external resistance of 0.1 Ω), and two external resistances, 0.1 and 10 Ω (at an HRT of 13.75 h) (Fig. 3.3). The HRT of 18 h resulted in the lowest conductivity of 4.52 ± 0.40 mS/cm in the brackish water, and a shorter
HRT of 6 h doubled the effluent conductivity to 9.35 ± 0.08 mS/cm. Accordingly, the energy consumption by the ED to desalinate the UMDC effluent increased from 1061 ± 64 J for the effluent at the HRT of 18 h to 2495 ± 276 J for the effluent at 6 h. Compared with the energy consumed by the ED treating brackish water without UMDC pre-desalination, the energy savings varied from more than 63.2 ± 2.2 % for the condition of HRT 18 h to 13.5 ± 9.6 % for the lowest HRT. Increasing the external resistance from 0.1 to 10 Ω at the HRT of 13.5 h also increased the effluent conductivity to 9.20 ± 0.28 mS/cm; consequently, the energy consumption by the ED treating this effluent increased to 2325 ± 51 J and energy savings decreased to 19.4 ± 1.8 %. It is worth noting that altering HRTs did not obviously change current generation and electric current of the UMDC at 0.1 Ω varied between 90 and 100 mA under three HRTs; however, increasing the external resistance to 10 Ω significantly decreased the current generation to ~38 mA.

Fig. 3.3 Effects of HRTs and external resistances on the UMDC performance and energy consumption in the ED.
3.3.2 Operating Conditions of the three-UMDC system

The operating conditions, high-current vs. high-power, were investigated with three UMDCs electrically connected either in series or in parallel at an HRT of 18 h. The ohmic resistance of the UMDC system was determined as 30 Ω (serial connection) or 5 Ω (parallel connection) using polarization curves (Fig. S1, Appendix 1); thus, the UMDC system was operated at the ohmic resistance as the high-power condition. The high-current condition was achieved with an external resistance of 0.1 Ω. In addition, the UMDC system was operated under the mode of charging a rechargeable battery or an ultracapacitor. The saline effluents collected from those operations were further desalinated by an ED.

![Current generation of the UMDC system in serial connection under different conditions.](image)

When three UMDCs were connected in series, the open circuit potential (OCP) reached 3.25 V (Fig. S1, Appendix 1). High OCPs (>1 V) have been reported in our previous studies of both
MFCs and MDCs. The maximum power output of the UMDC system was 72 mW and the short circuit current was 108 mA. During the 18-h test, the current generation with the high-current operation decreased from 94 to 66 mA because of the reduced salinity in the salt solution by desalination, while the high-power operation decreased the current from 57 to 37 mA (Fig. 3.4). Likewise, current generation under the charging mode also exhibited a decreasing trend, although there was a difference between charging the rechargeable battery and the ultracapacitor. When charging the rechargeable battery, the current profile was similar to that of the high-power operation, but current dramatically decreased to ~3.6 mA when charging an ultracapacitor during the 18-h period. Total coulomb output depended on current generation. The high-current operation produced the highest coulomb of 4611 C, and the ultracapacitor-charging operation yielded the lowest of 820 C. The total coulombs from the high-power and battery-charging operations were 2535 and 2150 C, respectively. The conductivities of the UMDC effluent under those four conditions are shown in Fig. 3.5. As expected, the lowest conductivity was achieved from the high-current operation that produced the highest current and coulombs among the four. When one liter of those effluents was further desalinated by the ED individually, the lowest energy consumptions (excluding the energy release from the rechargeable battery or ultracapacitor) were from the rechargeable battery-charging operation (3709 ± 592 J) and the high-current operation (3816 ± 79 J). When brackish water was fed continuously into the UMDC system, current generation was relatively stable at ~100 mA with the high-current operation, resulting in a low-effluent conductivity of 5.73 ± 0.14 mS/cm that consumed 2709 ± 649 J by the ED to desalinate one liter of this effluent.
The UMDC system in parallel connection produced an open circuit voltage of 1.14 V, a maximum power output of 62 mW, and a short circuit current of 230 mA (Fig. S1, Appendix 1). The effluent conductivities and the ED energy consumption under both high-current and high-power conditions were similar to those in the serial connection (Fig. S2, Appendix 1). The current generations under both conditions are shown in Fig. S3, Appendix 1. The pHs of the anode effluent and salt effluent under parallel connection were also similar to those under serial connection (Fig. S4, Appendix 1). Because charging with either rechargeable battery or ultracapacitor was not successful, no comparison was made for ED energy consumption under the conditions of the energy harvest for parallel connection.

3.3.3 Charging and Discharging
The charging and discharging of the electric energy produced in the UMDC system was examined with two different energy-storage units, a rechargeable battery, and an ultracapacitor.
Under the serial connection, current generations of the UMDC system with both energy storage units during the charging process are shown in Fig. 3.4. The charging voltages behaved differently: the voltage of the rechargeable battery was constantly at 1.2 V, while the voltage of the ultracapacitor increased from 0.34 to 2.67 V in 18 h (Fig. 3.6A). As a result, the total energy charged into the rechargeable battery was 2582 J, and there was 1248 J delivered into the ultracapacitor by the same UMDC system during the same period of time. For comparison, the UMDC system could produce 2983 J with the high power operation. Therefore, the rechargeable battery had extracted 86.6 % of the theoretic energy produced in the UMDC system and the ultracapacitor had a charging efficiency of 41.8 %. When the two energy-storage units were discharged at 3.3 V (via a DC-DC converter) to drive ED treating the effluents from the charging operation, the energy released was 1333 and 780 J from the rechargeable battery and the ultracapacitor, respectively. Thus, the discharging efficiency of the rechargeable battery was 51.6 % and the ultracapacitor discharged 62.5 % of its stored energy. The difference was also shown in the discharging time (Fig. 3.6B). The overall energy recovery efficiency was 44.6 % for the rechargeable battery and 26.1 % for the ultracapacitor.

The parallel connection did not achieve a comparable charging to the serial connection. Because the voltage of the UMDC system under parallel connection was low, a DC-DC converter was linked to the system to boost the voltage for charging. After 18-h charging, the voltage of the ultracapacitor reached 0.72 V (Fig. 3.6A), representing an energy content of 91 J, significantly lower than 1248 J from the serial connection charging. The battery charging (two rechargeable batteries connected in series) was not successful. No discharging test was performed with either ultracapacitor or rechargeable batteries because low energy extraction from the UMDC system
under the parallel connection.

![Voltage curves of an ultracapacitor (350 F, 2.7V) charged by the UMDC system in serial and parallel connections (A) and current productions in the ED powered by the rechargeable battery and the ultracapacitor with the serial UMDC operation (B).]

3.4. Discussion

This study has demonstrated experimentally and quantitatively the energy benefits of using MDCs as pre-desalination units before EDs, although the conclusion is straightforward. The lower salinity of the UMDC effluent reduced both energy consumption and desalination time by
the ED. Current, or electron flow, is the key factor to salt removal in MDCs. Although previous studies suggested that salinity reduction in MDCs was caused by multiple factors, including current, diffusion, ion exchange, and water osmosis, current generation is the most important among them \(^{44,46}\). A higher current improved salt removal, as indicated by the comparison of desalination results between 0.1 and 10 Ω at the same HRT; however, the effluent salinity is determined by both current generation and total salt input. A higher salt input tends to cause a higher effluent salinity, which explains why different effluent salinities were obtained at 0.1 Ω, although current generation was similar among three HRTs. It also explains why the desalinated waters at two different current generations (0.1 Ω/HRT 6 h and 10 Ω/HRT 13.75 h) had a similar effluent conductivity, even though more salts were actually removed under the condition of 0.1 Ω/HRT 6 h.

The low energy requirement by the ED treating UMDC effluents under the charging-battery condition (serial connection) suggests that high-power operation could be beneficial because of the produced energy, confirming the finding in our previous publication, which theoretically analyzed the energy benefits of high-power operation with reverse-osmosis as a post-desalination process \(^{46}\). This result could be attributed to the use of a NiMH rechargeable battery with an operating voltage of 1.2 V, very close to the UMDC voltage of 1.5 V where the maximum power output was achieved. A similar current generation between the charging-battery and high-power conditions (Fig. 3.4) also indicated that the rechargeable battery was charged under a condition similar to high-power production. Thus, charging this battery could extract most of the UMDC energy (86.6% in the present study). The results have revealed that bioenergy produced in MDCs could be potentially useful. High-current operation, on the other hand, does not require energy
transfer and thus simplifies the system operation. Although the energy requirement with the high-current operation did not outperform that of the charging-battery condition in batch (brackish water) operation, continuous feeding of brackish water with the high-current operation led to a lower energy requirement by the ED. If the discharging efficiency of the rechargeable battery can be improved beyond 52% of the present study (which seems likely 54), high-power operation will be more advantageous. When the efficiency of energy-storage units is low, the simple system with high-current operation (no need of charging and discharging) should be considered because it can save capital investment in infrastructure and energy-storage units.

A critical element in high-power operation is the transfer, storage, and use of electric energy produced from MDCs, and several losses of energy are involved in this process. The actual charging condition has a current generation lower than high-power operation; therefore, energy is lost during the charging process. In this study, the rechargeable battery could extract more than 86% of the energy, but the ultracapacitor could only achieve 42%. Energy loss during storage can be minimized, assuming brief storage is needed (longer storage time will increase the loss of electric charge due to self-discharge). Another major loss occurs during discharging; although the rechargeable battery obtained the most of energy from the UMDC system, it lost nearly 50% during the discharging through powering ED operation. A efficient electric storage unit and circuit may help to reduce this loss, and it is found that the discharging efficiency of some energy-storage units can be more than 60% 54.

The charging/discharging issues are important to the high-power operation of MDCs and could also have some implications for MFCs, which are designed to produce electric power. The
research on MFC charging has been limited to power delivery from sediment MFCs \(^{55-56}\), but there is a significant difference of energy harvest between sediment MFCs and reactor-type MFCs for wastewater treatment. The goal of power production in sediment MFCs is to support remote sensors that require low power input. Energy loss is acceptable and not a critical issue during the process of storage and use, as long as it can accumulate enough energy within a designed period of time. Reactor-type MFCs, on the other hand, are expected to deliver as much power as possible, and energy loss should be minimized. In previous studies, power management systems (PMS) were usually employed to extract energy from MFC \(^{52,56}\), but a significant energy loss occurred, for example, in which only 15% of the energy from an MFC could be used to power a hydrophone, possibly due to the low efficiency of the charge pump \(^{57}\).

The direct charging (in serial connection of the UMDCs) and use of a DC-DC converter to discharge in our study yielded the overall energy recovery efficiency between 26.1% and 44.6 %, with an inferior performance from the ultracapacitor, which could be due to a large self-discharge during the charging process. Ultracapacitors are designed for quick charging (from seconds to minutes vs. hours of charging batteries). The low electricity production in the UMDC system resulted in a long charging-period in hours and thus could have increased energy loss in the ultracapacitor via self-discharge. Therefore, according to the results of the present study, rechargeable batteries may be more appropriate for extracting energy from reactor-type bioelectrochemical systems. The indirect charging with the aid of a DC-DC converter (in parallel connection) did not successfully charge either the ultracapacitor or rechargeable battery, indicating that the DC-DC converter may have consumed a large amount of electric energy \(^{58}\). However, a power management system (including a DC-DC converter) may still be necessary for
harvesting energy from large-scale bioelectrochemical systems, in which the energy loss to a power management system could be insignificant compared with energy production.

Considering that MDCs do not require external energy to run desalination, except the energy for pumping at a normal pressure, the use of MDCs as pre-desalination units could save a considerable amount of energy; however, challenges remain in developing a well-functioned MDC-ED system. First, MDC performance should be further improved. The results clearly indicate that better-performing MDCs can save more energy because more salt is removed before EDs. Second, the MDC-ED system requires a supply of wastewater; therefore its application is limited to the areas that have access to both wastewater and brackish water. The use of organic compounds, instead of wastewater, to feed the anode of MDCs could make the system more flexible, but its economic feasibility needs investigation. Third, it requires coordinating the operation between MDCs and EDs; for example, in this study, the desalination process in the UMDC was much slower than that of the ED (18 h vs. 1-3 h for treating the same amount of water), causing the ED to be on standby most of time. This problem may be solved by increasing the volume of MDCs or using MDCs to desalinate a portion of feeding water. Last, when evaluating MDCs, one should have the wastewater treatment as a primary goal and desalination as a beneficial addition.

3.5. Conclusion
The results demonstrated that using UMDCs as a pre-desalination process saved both energy and desalination time in the ED. Bioenergy was harvested from the UMDCs and applied to power the ED. The MDC-ED system could be potentially applicable with further improvement of MDC
performance and optimized coordination between those two processes.

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Chapter 4 Osmotic Microbial Desalination Cell

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4.1 Introduction
Desalination is an important approach to producing drinking water, especially for some areas where seawater is readily available but freshwater sources are limited. Generally, desalination can be accomplished using thermal and membrane technologies, both of which have been commercialized. Thermal technology uses heat to vaporize water, thereby realizing the separation of salts from water. The common thermal methods are multi-effect distillation, multistage flash distillation, and vapor compression.\(^{59}\) Membrane technology driven by electric energy includes reverse osmosis, membrane distillation, and electrodialysis.\(^{39}\) The extensive consumption of energy by desalination technologies is still a drawback and results in high operating costs and water prices. The shortage of clean freshwater sources and the high cost of current desalination processes create a strong need for new desalination technologies with environmental and economic benefits.\(^{38}\)

Recent development of a microbial catalyzed desalination system called microbial desalination cell (MDC) has garnered a great deal of attentions and been studied for different configurations, operations and functions.\(^{7}\) An MDC takes advantage of microbial metabolism in its anode for generating an electric driving force that stimulates ion migration from its middle chamber into the anode (anions) and the cathode (cations), respectively. As a result, salinity in the middle chamber can be greatly reduced.\(^{9-10,12}\) Because the driving force of desalination comes from microbial activities (bioelectricity), it is expected that MDC desalination will be a slow process;
therefore, it is more appropriate to function as a pre-desalination process before conventional desalination units. It is known that electricity production is the dominant factor for salt removal in an MDC; however, other factors such as salt diffusion and water osmosis have also been discussed. Water migration into the middle chamber via osmosis is of particular interest because it will not only dilute saline water but also increase water production. Moreover, if the added water is from anolyte (i.e. wastewater), then it will reduce the discharge of wastewater effluent and comes with beneficial water reuse. Therefore, an active osmosis is desired to extract water from the anode to dilute saline water and achieve both lower salinity and water recovery.

The active water osmosis can be accomplished by forward osmosis (FO) process, in which the FO membrane allows the free passage of water molecules from a higher water potential to a lower water potential. The movement of ions across the FO membrane is mostly rejected. FO technology has been studied for producing reusable water from wastewater, landfill leachate, and digester concentrate. It has also been used for seawater desalination, the pharmaceutical industry, food processing, and the production of osmotic electric power.

Our previous work has successfully integrated FO into a bioelectrochemical system to form a novel osmotic microbial fuel cell (OsMFC). The OsMFC could bring down the conductivity of the catholyte (draw solution) through dilution with water flux from the anode, while produce bioelectricity from organic oxidation. Water flux accelerated proton transport and thus increased current generation, compared with a conventional MFC. The total dissolved solids in the
catholyte did not obviously change, although its concentration decreased due to the increased water mass.

4.2 Methods and Materials
In this study, we have extended the concept of the OsMFC to MDC technology, and created an osmotic microbial desalination cells (OsMDC). The anion exchange membrane (AEM) that separates the anode and the middle chamber in a conventional MDC was replaced by an FO membrane in the OsMDC; and a cation exchange membrane (CEM) was still used between the cathode and the middle chamber (Fig. 4.1). With such a change, high-quality water can be extracted from the anode through FO process to dilute the saline water in the middle chamber, which will also be desalinated via electricity generation, similar to that in a conventional MDC. The feasibility of the OsMDC was examined under different operating conditions and salinities. It was also compared with a conventional MDC in terms of desalination and water production. To ensure that the OsMDC performance was not limited by the reactions in the anode and cathode, we oversupplied organic substrates to the anode and used potassium ferricyanide as a terminal electron acceptor in the cathode (more details in the Appendix 2).
Fig. 4.1 Schematic of an osmotic microbial desalination cell consisting of forward osmosis membrane (FO) and cation exchange membrane (CEM).

4.3 Results and Discussions
First, we examined the OsMDC desalination under the conditions of the open and the closed circuits, respectively. Because no electricity would be produced, the open circuit mimicked an FO process; the closed circuit was operated for high current generation (at a low external resistance of 1 Ω) because more electron movement will result in more salt removal. In an operating cycle of three days and at an initial salt concentration of 10 g NaCl/L, both conditions had successfully extracted water from the anolyte with a higher water production (in the middle chamber) under the open circuit (Fig. 4.2A). The water flux at the end of three days was 0.42 ± 0.01 LMH and 0.29 ± 0.04 LMH for the open and the closed circuits, respectively. It should be noted that a higher water flux occurred in the early stage and it decreased over the time due to the decreased salinity (osmotic pressure). For instance, at the end of the first day, both conditions achieved a similar water flux (0.65 ± 0.05 LMH and 0.69 ± 0.01 LMH). The water flux diluted the saline water and thus reduced its conductivity (salinity) in both conditions. The closed circuit had a much lower conductivity of 6.5 ± 1.1 mS/cm, about 62% reduction from the initial conductivity of 17.1 mS/cm, compared with 11.5 ± 0.2 mS/cm under the open circuit that was about 33% reduction (Fig. 4.2B). The difference in salinity reduction between the two conditions suggested that dilution was not the only factor that caused salinity decrease under the closed circuit. This was also supported by a theoretic estimation of dilution effect on conductivity reduction assuming that water flux was the only factor under the closed circuit, in which the final conductivity with dilution effect only would be 13.1 mS/cm, about twice the actual final conductivity. The additional factor under the closed circuit was electricity generation.
At an external resistance of 1 Ω, the OsMDC produced an average current of 4.6 mA during three days. The electricity production required ions movements across the membranes and led to desalination. With the information of the total water volume (Fig. 4.2A) and the conductivity (Fig. 4.2B), we calculated the mass of total NaCl remained in the saline water (Fig. 4.2C). The results clearly showed that a significant salt removal (57.8%) occurred with the closed circuit, while the open circuit had a slightly decrease (3.4%) in the salt mass after three-day operation (Fig. 4.2C). This difference demonstrated that the salinity reduction in an OsMDC under the close circuit was caused by both water dilution and electric current with the latter playing a major role. Compared with the FO process (the OsMDC under the open circuit), the OsMDC has advantages in salt removal and producing a lower salinity, which will benefit the downstream desalination when it acts as a pre-desalination unit.
Fig. 4.2 Comparison of the OsMDC performance between the open and closed circuits: (A) water production in the middle chamber, (B) the conductivity of the saline water and (C) the mass of total NaCl calculated from the mass of water and the conductivity.

We then investigated the effects of salinities on the OsMDC performance, and compared it with a conventional MDC that had the AEM between the anode and the middle chambers. A higher salinity resulted in more water extraction because of a higher osmotic pressure (Fig. 4.3A). With the initial concentration of 20 g NaCl/L, the water flux decreased from 1.46 ± 0.06 LMH (day one) to 1.01 ± 0.01 LMH (day three). The lowest initial salinity of 5 g/L produced 0.15 ± 0.04 LMH in day one and a negative water flux of -0.06 ± 0.05 LMH at the end of three days, because
the salinity decreased to a level lower than that of the anolyte and reverse water flux happened. The conductivity was reduced with all three tested salt concentrations (Fig. 4.3B) and the reduction rate varied between 51.4% (5 g/L) and 62.0% (10 g/L). The reduction of salt mass behaved very differently: the OsMDC achieved 65.9% and 57.8% of salt removal for the initial concentrations of 5 and 10 g/L, and only 17.7% of salt reduction with 20 g/L (Fig. 4.3C). Considering the fact that current generation with those three initial salt concentrations was similar (data not shown) but water flux was very different, we concluded that the salinity reduction with low initial concentration (5 and 10 g/L) was mainly due to salt removal by electricity generation, while with a higher initial concentration (e.g., 20 g/L), dilution (water flux) was the major contributor to salinity decrease.

The comparison between the OsMDC and the MDC (Fig. 4.3) indicated that the OsMDC was advantageous in water extraction and salinity reduction, but not in salt removal. No water flux into the middle chamber was observed in the MDC with all three initial salt concentrations (Fig. 4.3A); in fact, slightly negative water flux occurred, possibly because of a higher salinity in the catholyte that caused water osmosis from the middle chamber to the cathode chamber. The MDC produced a lower final conductivity than the OsMDC when the initial salt concentration was low (5 and 10 g/L) (Fig. 4.3B). With 5 g/L, the MDC reduced the salinity to 0.1 ± 0.0 mS/cm in two days. However, at the higher initial salt concentration of 20 g/L, the MDC generated a final salinity of 19.2 ± 1.3 mS/cm, higher than 13.1 ± 0.6 mS/cm in the OsMDC. The MDC outperformed the OsMDC in salt removal with all three salt concentrations (Fig. 4.3C). The electricity generation in the MDC was similar to that in the OsMDC (data not shown). The final
pH of the saline water in the OsMDC varied between 6.5 and 7.0, lower than 8.0 in the MDC, because that the water flux promoted proton transport from the anode into the middle chamber.  

To understand why the OsMDC did not have a good salt removal, we analyzed the mass of the individual ions in the saline water. Three ions including two cations (Na+ and K+) and one anion (Cl-) were detected and quantified (Fig. 4.4). Initially, there were only two ions, Na+ and Cl-, in the saline water with the same molar mass (1:1). After the three-day operation, the ratio between two ions became 1:1.5-1.9, suggesting that sodium ions were removed more quickly than chloride ions. In theory, both ions should be removed at the same rate because the transfer of every electron from the anode electrode to the cathode electrode should drive one sodium ion to move into the cathode and one chloride ion to migrate into the anode. This imbalance in ions removal was likely due to the FO membrane that retarded chloride ions passing through. Unlike an AEM that allows only anions to move through, an FO membrane does not selectively transport ions and it has a high rejection of a wide range of ions. As a result, sodium ions moved through the CEM into the cathode driven by electron flow but chloride ions could not transport via the FO membrane at the same step.
Fig. 4.3 The effect of the initial salinity on the OsMDC performance and the comparison between the OsMDC and the MDC: (A) water volume, (B) conductivity, and (C) salt mass.
The imbalanced charge required additional cations into the middle chamber and those cations could come from both the anode and the cathode chambers. Although the water flux accelerated proton transport from the anode into the middle chamber, the quantity of protons was not sufficient to balance the charge. The intrusion of potassium ion from the cathode contributed to the charge balance and the molar mass of K+ measured in the saline water makes the ratio between cations and anions close to 1:1 (Fig. 4.4). The catholyte contained a large amount of potassium ions from potassium ferricyanide and potassium phosphate buffer, which facilitated K+ movement. However, ion movement between the anode and the middle chamber is still required for electricity generation. Because the transport of chloride ions and protons was not sufficient to support electricity generation, there might be movement of cations from the anode into the middle chamber, too. One candidate of such cations is sodium ion. The anolyte contained sodium ions from sodium acetate, sodium chloride and sodium bicarbonate. Both water flux and electricity generation could drive sodium ions to leave the anode and migrate into the middle chamber. We did not monitor the sodium concentration in the anode because it (with acetate) was maintained at a high concentration; therefore, the pathway of cation movement from the anode to the middle chamber needs further verification.
In general, we believe that there are active transport and/or exchange of cations between the anode/cathode chambers and the middle chamber in the OsMDC, and this movement might have decreased the charge transfer efficiency. For example, at the initial salt concentration of 10 g/L, the total charge (coulomb) produced in three days was about 1225 C, which is almost enough to remove all the salt (NaCl) that requires 1237 C. The actual removal efficiency (and the charge transfer efficiency) was less than 60%, indicating that some electrons generated in the anode were not used to drive salt out of the middle chamber. It is likely that the cation movement into the middle chamber contributed to current generation, as well as the salt mass.
It seems that the OsMDC will be more suitable for treating high salinity waters because of a stronger water flux for dilution effect. Seawater that comes from natural sources contains a higher salinity (than the saline water tested in this study) and is widely used for desalination. Therefore, we examined the desalination of artificial seawater (prepared with aquarium sea salts) in the OsMDC (Fig. 4.5). In a cycle of three days, the seawater conductivity decreased from 46.7 mS/cm to 17.1 ± 4.4 mS/cm, more than 60% of reduction. The final volume of the seawater was 162.3 ± 1.2 mL, twice the initial volume of 75.1 mL, and the water flux changed from 1.30 ± 0.01 LMH (day one) to 0.96 ± 0.01 LMH (day three). This water flux is slightly lower than the one with 20 g NaCl/L, possibly due to the complex elements in seawater that could result in a more serious membrane fouling than NaCl. We measured the membrane resistance using electrochemical impedance spectroscopy and the Bode plots showed that the fouled membrane (after 10-day seawater operation) behaved clearly different from the new membrane (Fig. S3, Appendix 2). The overall impedance increased due to the fouling, and the ohmic resistance (the impedance at the high frequency) increased from 12.5 to 13.9 Ω. The FO membrane fouling has
been a subject of study and chemical and/or mechanical methods are developed to restore the membrane function \(^{71-72}\). The future OsMDC development will take advantage of the existing knowledge on membrane fouling and evolve a cleaning method (with less effects on the anode microbes) to alleviate fouling condition.

Those results have collectively demonstrated that the OsMDC could be a promising technology for the integrated wastewater treatment, desalination and water reuse, with environmental, energy and economic benefits. Compared with the FO technology, the OsMDC can convert organics into electric energy and remove salts from saline waters. Compared with the MDC technology, the OsMDC can recover high-quality water from wastewater and reduce salinity through dilution; in addition, according to the manufacturers, the FO membrane in the OsMDC has a lower cost ($30/m2) than the AEM used in the MDC ($97/m2), which will greatly reduce the capital investment. Before stepping into practical issues like reactor configuration and scaling up, further investigation is required to gain the understanding of the fundamental issues such as ion transport and membrane fouling.

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Chapter 5 Improving Water Desalination and Wastewater Treatment by Hydraulically Coupling an Osmotic Microbial Fuel Cell with a Microbial Desalination Cell

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Abstract

An innovative treatment system consisting of two membrane-based bioelectrochemical reactors was developed to treat artificial wastewater and desalinate saline water. In this system, an osmotic microbial fuel cell (OsMFC) containing a forward-osmosis (FO) membrane was hydraulically coupled with a microbial desalination cell (MDC) that had ion exchange membranes. The coupled system significantly improved desalination efficiency through both dilution (in the OsMFC) and salt removal (in the MDC), and achieved more organic removal than an individual MDC. It was found that the high-power operation mode was more suitable for the OsMFC than the open-circuit mode and the high-current mode, because of good desalination performance (95.9% conductivity reduction in the coupled system) and energy production (0.160 kWh/m³ treated saline water). When the active layer of the FO membrane was facing the feed solution, more water flux was obtained than the reversal membrane orientation. The coupled system achieved high reduction of conductivity (>90%) from the salt solution containing 10-50 g NaCl/L. The acidified water was more advantageous as a catholyte for the MDC because of the superior desalination performance. These results have collectively demonstrated the feasibility of a membrane-based bioelectrochemical system for simultaneous wastewater treatment and saline water desalination.
5.1. Introduction
Water is a vital resource to human beings; freshwater shortage and pollution has become a crucial problem that seriously affects a large population of people and our environment. To alleviate this problem, wastewater must be effectively treated before being discharged and new freshwater sources must be identified, for instance, through desalinating seawater or brackish water. However, the existing technologies for wastewater treatment (mainly based on aerobic processes) and desalination (e.g., reverse osmosis and distillation) are energy intensive associated with high operating expense. Alternative approaches such as anaerobic treatment of wastewater and desalination driven by renewable energy have received more and more attention. In addition, wastewater treatment and saline water desalination are conducted primarily in distinct and separated approaches (and different locations). This separation could lead to long-standing inefficient use of land and human resources. Therefore, it will be of great interest to develop a treatment system integrating wastewater treatment and saline-water desalination.

Microbial desalination cells (MDCs) are an emerging concept to accomplish simultaneous wastewater treatment and saline-water desalination in a single reactor. In an MDC, saline water is fed into the middle chamber, which is separated from the anode chamber by anion exchange membrane (AEM) and from cathode chamber by cation exchange membrane (CEM). Electrochemically-active bacteria in the anode oxidize organic substrates and release electrons, which move to the cathode to reduce terminal electron acceptors (e.g., oxygen). To maintain electroneutrality, cations in the saline solution will migrate through CEM into cathode chamber and anions will migrate through AEM into anode chamber. In this way, saline water in
middle chamber is desalinated. Efforts from different perspectives have been made to improve MDC technology towards practical application. The configuration of MDCs is designed as tubular or stacked reactors for continuous operation \(^{45-48}\). When an additional electrical potential is applied to an MDC, hydrogen can be produced in cathode chamber \(^{49-50}\). Recently, ion exchange resins were added into the salt chamber of an MDC to enhance desalination performance when treating brackish water with low salinity \(^{76-77}\).

In our previous study of MDCs, we observed water flux into the middle chamber caused by salinity gradient; the additional water lowered the salinity \(^{46}\). This finding intrigued us to seek active water flux into salt chamber for reducing salinity, which was realized in our newly developed osmotic microbial fuel cells (OsMFCs) through integrating forward osmosis (FO) into MFCs \(^{78}\). FO is a process in which water molecules migrates from one side of an FO membrane with higher water chemical potential to the other side of FO membrane with lower water chemical potential, while the migration of ions (such as Na\(^+\) and Cl\(^-\)) is rejected \(^{79-80}\). By replacing the CEM with an FO membrane, the OsMFC could extract water from the anolyte, thereby improving water reuse from wastewater, and electricity generation in an OsMFC was higher than a conventional MFC containing CEM, demonstrating that OsMFCs effectively inherit the features of both MFCs and FO technologies. We have obtained better understanding of OsMFCs through examining the effects of different draw solutes on their performance and conducting a long-term operation with actual wastewater \(^{81-82}\). The FO concept was also applied to MDC technology (to form an OsMDC); however, the presence of an FO membrane prevented salt transport and thus resulted in a lower salt reduction than a conventional MDC, although at 20 g TDS/L the OsMDC produced a lower salinity effluent because of the dilution with water flux.
The application of OsMFCs for water reuse (in wastewater treatment) would require recycle of draw solution and a post-treatment, which will increase the operating cost and decrease the viability of the technology. The draw solution that does not need to be recycled, such as seawater and saline wastewater, will be more preferable. Recent development of OsMFCs adopted an air cathode configuration and attempted to simplify the reactor operation by omitting aeration.

We have previously proposed to hydraulically link OsMFCs to MDCs (Fig. 5.1), in which an OsMFC is used to reclaim water from wastewater and an MDC is employed to remove salt. The recovered water in the cathode of the OsMFC can reduce the conductivity of saline water that is used as both draw solution and catholyte. Although reverse salt flux would occur in an OsMFC, major salt removal is not expected in this step. The catholyte (salt effluent) from OsMFC is fed into an MDC, in which salt will be removed through desalination. Meanwhile, wastewater is treated in both anodes of OsMFC and MDC, and provides electrons for electricity generation. In this study, we experimentally studied the proposed system operated at a room temperature with the objectives to demonstrate its feasibility and influence factors such as membrane orientation, OsMFC operating conditions and salt concentrations.
5.2. Experimental

5.2.1 OsMFC setup and operation
The OsMFC was made of two pieces of polycarbonate blocks joined together by steel rods and bolts. One piece of FO membrane (Hydration Technology Innovations, Albany, OR) with dimension of 17cm x 11cm was used as separator between the anode and the cathode compartments. The same membrane was used during the entire course of experiments. The liquid volumes of the anode and the cathode compartments were 330 mL/each. The anode electrodes were carbon brush and the cathode electrode was a piece of carbon cloth coated with platinum as oxygen reducing catalyst (~ 0.5 mg Pt/cm$^2$). The cathode compartment was aerated with air by an aquarium air pump.

The anode of the OsMFC was fed with a synthetic solution (artificial wastewater) containing (per L of tap water): sodium acetate, 1 g; NH$_4$Cl, 0.15 g; NaCl, 0.5 g; MgSO$_4$, 0.015 g; CaCl$_2$, 0.02 g;
KH$_2$PO$_4$, 0.53 g; K$_2$HPO$_4$, 1.07 g; yeast extract, 0.1 g; and trace element, 1 mL. The anolyte was fed at 8 mL/min, resulting in a hydraulic retention time (HRT) of ~0.7 h in the OsMFC and ~2.3 h in the MDC; therefore the overall anolyte HRT in the OsMFC/MDC system was 3 h. The anolyte in OsMFC was recirculated at 150 mL/min. The initial anode inocula were a mixture of aerobic and anaerobic sludge from South Shore Wastewater Treatment Plant (Milwaukee, WI). The catholyte for the OsMFC was prepared by dissolving sodium chloride in tap water and was pumped into the OsMFC at a flow rate of 0.14 mL/min by a peristaltic pump (Cole-Parmer, Vernon Hills, IL, USA). The catholyte HRT of in the OsMFC cathode was 1.6 d.

Two FO membrane orientations, which are Pressure Retard Osmosis (PRO) mode and Forward Osmosis (FO) mode, were investigated in this study. In the PRO mode, the support layer of the FO membrane was orientated towards feed solution and active layer was against draw solution; while in the FO mode, the above orientation was reversed. In addition, three different operation modes of the OsMFC were also studied for different current generation. In the first and second mode, the OsMFC was operated in high power condition (in which the external resistance was set equal to its internal resistance) and high current condition (with an external resistance of 1 Ω); while in the third mode, OsMFC was operated under an open circuit condition that had no current production. Finally, the OsMFC were operated with three different catholyte salinities, 10, 35 and 50 g NaCl/L.
5.2.2 MDC setup and operation
A tubular MDC was established similarly to our previous study \(^4^6\), and operated under a high-current condition (external resistance at 0.1 \(\Omega\)). The MDC consisted of two membrane tubes, an anion exchange membrane (AEM, Membrane International, Inc., Ringwood, NJ, USA) surrounding the anode compartment, and a cation exchange membrane (CEM, Membrane International, Inc.) wrapping the salt compartment \(^4^5\). The cathode was exposed to the air and rinsed by acidified water (pH 2.5 adjusted with sulfuric acid) at a flow rate of 4 mL/min. The anode liquid volume was 1100 mL and the salt chamber volume was 850 mL. The anode electrode was a carbon brush and the cathode electrode was carbon cloth with 0.5 mg/cm\(^2\) of Pt as catalyst. Although phosphate buffer solution (PBS) is more widely used in bioelectrochemical studies, previous research from our group shows that acidified water could also provide satisfactory performance at a cost of 3\% of that using PBS.

The anolyte of the MDC was the anode effluent from the OsMFC. The influent into the salt compartment of the MDC was the cathode effluent of the OsMFC, which was first collected in a test tube and then pumped into MDC salt compartment at a flow rate of 0.3 mL/min for desalination. The HRT of salt solution in the MDC was 1.9 d, resulting in a total salt solution HRT of 3.5 d for the coupled system.

5.2.3 Measurement and analysis
The voltages were recorded every 3 min by a digital multimeter (2700, Keithley Instruments, Inc., Cleveland, OH, USA). The pH was measured using a benchtop pH meter (Oakton Instruments, Vernon Hills, IL, USA). The conductivity was measured by a benchtop conductivity
meter (Mettler-Toledo, Columbus, OH, USA). The polarization curve was performed by a potentiostat (Reference 600, Gamry Instruments, Warminster, PA, USA) at a scan rate of 0.2 mV/s. Chemical oxygen demand (COD) was measured using test kit from Hach Co. (Loveland, CO USA) according to the manufacture manual. The salt removal rate (kg/m³/d) was calculated as the difference between the salt input and output of the MDC per day and per cubic meter of the MDC salt compartment. Columbic efficiency (CE) was calculated as:

\[
CE = \frac{Q_{\text{output}}}{Q_{\text{input}} - r} = \frac{\sum I(A) t (s)}{96485 (\frac{C}{mol e^-}) \times COD_{\text{removed}} (mol) \times 4 (\frac{mol e^-}{mol O_2})}
\]

where \(Q_{\text{output}}\) is the produced charge, \(Q_{\text{input}} - r\) is the total charge available in the removed organic compounds, \(I\) is electric current and \(t\) is time. \(COD_{\text{removed}}\) is the amount of the removed COD within time \(t\). The removed COD was also expressed in percentage as a ratio of initial COD input and final COD remained.

5.3. Results and discussion

5.3.1 General performance of the coupled system

The coupled system was operated in the laboratory for more than six months, and no major cleaning of both ion exchange membrane (in the MDC) or FO membrane (in the OsMFC) was conducted during the test. To demonstrate the benefit of this linkage, the performance of the coupled system was compared with that of a single MDC at two different (salt solution) HRTs. The MDC-1 had the same HRT (1.9 d) as the MDC in the coupled system, and the MDC-2 had an HRT equal to the total salt solution HRT (3.5 d) of the coupled system (including both OsMFC and MDC). At an initial conductivity of 53.5 mS/cm (35 g NaCl/L), the MDC-1 produced an effluent of 29.2±0.6 mS/cm and the MDC-2 had a final conductivity of 27.4±1.47
mS/cm, both of which were significantly higher than 2.2±0.5 mS/cm of the coupled system (Fig. 5.2), suggesting that adding an OsMFC as a pre-treatment process before an MDC greatly benefited salinity reduction. This improved salinity reduction was mainly due to dilution by osmotic water flux from the anode compartment into the cathode compartment in the OsMFC: the cathode effluent was more than twice its influent.

![Graph showing conductivity and COD removal](image)

Fig. 5.2. The final conductivity and COD concentration in the coupled system compared with individual MDC at two different HRTs.

A key function of the coupled system is wastewater treatment, and thus organic removal is another important parameter to evaluate the system performance. As expected, the coupled system had more COD removal (>85%) and a lower effluent COD concentration of 126±33.9 mg/L. Because the volume of the anode solution decreased due to water loss to the cathode compartment (as a result, the COD concentration was “concentrated”), the actual organic reduction was even higher. The effluents from the single MDC contained higher COD of 129.3±15.1 mg/L and 164.7±46.1 mg/L for the MDC-1 and the MDC-2, respectively. The improved organic removal in the coupled system was attributed to the additional organic oxidation in the anode of the OsMFC, which could be used to control organic supply to the...
MDC. This control is potentially critical to the following MDC desalination and the overall system performance, because an insufficient organic supply will not provide enough electrons to drive salt removal in the MDC and thus decrease the desalination efficiency, but an oversupply of organics to the MDC will result in more organic residue in the MDC effluent (or final effluent), thereby deteriorating the effluent quality.

Because of the important role of the OsMFC in the whole system, the following sections attempt to understand the key factors that affect the system performance and focus on three aspects of the OsMFC, FO membrane orientation, current generation and salt concentrations. The MDC, on the other hand, was always operated under a condition of high current generation, because more electron flow drives more desalination.

5.3.2 Operation modes
Because the MDC was always operated under a condition for the maximal current generation (for better salt removal), it was of interest to investigate the effect of the OsMFC operation on the system performance. Three operation modes (with FO membrane orientation) including high-power, high-current and open-circuit, were investigated. The high-power mode was conducted at an external resistor of 31 Ω, which determined close to the internal resistance of the OsMFC by a polarization test. The maximum power density obtained from the polarization test was 12.45 W/m³, but the actual power density in the high-power mode (operated at 31 Ω) was 2.41 W/m³, because polarization measurement could overestimate the power output in an MFC. The
high-current mode was conducted at external resistance of 1 Ω. The open-circuit mode contained infinite external resistance and thus there was no current flow.

Fig. 5.3. The performance of desalination (conductivity reduction and salt removal rate) and organic reduction (COD removal and coulombic efficiency) of the coupled system (OsMFC+MDC) at three operation modes of the OsMFC (high power–black color, high-current–red color, and open circuit–green color).

The current generation in the OsMFC was obviously affected by the operation modes. While no current flowed in the open-circuit mode, the average current in the high-power mode and the high-current mode were 5.06±0.09 mA and 12.92±1.71 mA, respectively (Table 1). Based on the volume of the treated saline water, the energy production in the OsMFC was 0.094 kWh/m$^3$ in the high-power mode. The high-current mode produced an energy density of 0.019 kWh/m$^3$, and there was no energy production in the open-circuit mode. Meanwhile, the MDC produced 0.043 and 0.057 kWh/m$^3$ in the OsMFC high-power and high-current modes, respectively, resulting in a total energy production in the coupled system of 0.245 and 0.082 kWh/m$^3$ in those two modes. The MDC in the OsMFC open-circuit mode produced 0.041 kWh/m$^3$, which was also the total energy production of the coupled system in that mode. Clearly, the high-power mode of the OsMFC benefited the overall energy production, and the energy production in the OsMFC was
almost five times the one in the followed MDC. The organic removal in the coupled system was comparable among three operation modes. The overall COD removal efficiency varied between 82 and 86\% (Fig. 5.3), and the COD removal rate by the integrated system was 5.92-6.15 kg COD/m$^3$/d. About 20-30\% of COD removal occurred in the OsMFC (Table 5.1), and the rest (the majority) was conducted in the MDC (Table 5.2). In the OsMFC, the high-current condition resulted in the highest COD removal of 27.2±1.3 \% or 8.4±0.4 kg COD/m$^3$/d, and the open-circuit condition achieved the lowest, confirming that current generation can stimulate the oxidation of organic compounds in the anode of an MFC.\textsuperscript{53} However, the open-circuit condition still removed 21.2±3.0\% of COD or 6.6±0.9 kg COD/m$^3$/d, indicating that a large amount of COD removed in the OsMFC was not associated with electricity generation, which was also demonstrated by a low CE of 1.4-3.7\% in the OsMFC under the high-current or the high-power conditions. This low CE was partially due to the high organic loading rate, which was beyond what electrochemically-active organisms could handle but could still greatly reduced by other co-existing organisms in the anode community. Because of the high current generation in the MDC, the overall CE of the coupled system was 5-7\%.

The operation modes affected the reduction of conductivity of the saline water (Fig. 5.3). The highest reduction of 96.6±0.4\% occurred at the open-circuit mode, while the lowest of 86.6±1.9\% was obtained at the high-current mode. Likewise, the open-circuit mode achieved the highest salt removal of 8.13±0.08 kg/m$^3$/d, and the high-current mode yielded the lowest rate of 5.99±0.27 kg/m$^3$/d. Although water flux did not exhibit a trend like conductivity reduction and salt removal, the high-current mode still had the lowest water flux of 0.63±0.08 LMH among the three modes (Table 5.1). The high salt removal rate and high current generation in the MDC
under the open-circuit mode of the OsMFC was likely due to the high organic concentration in the OsMFC effluent (or the MDC influent) that provided more electrons for desalination in the MDC. The reason why the high-current mode had a lower water flux was possibly related to current generation and reversal salt flux: current generation requires ion transport between the anode and the cathode, and in an OsMFC it is possible that chloride ions move from the cathode into the anode through FO membrane because of the high NaCl concentration in the cathode; as a result, the difference of the osmotic pressure between the two compartment decreases, thereby reducing water flux. It has been demonstrated that salt can move reversely from draw solution to feed solution in an FO process\textsuperscript{87-88}, and current generation in an OsMFC could accelerate this process but further evidences are required to interpret this phenomenon. To conclude, the high-current mode may not be suitable for the OsMFC operation. The open-circuit mode led to the best desalination performance (slightly better than the high-power mode), but the OsMFC did not produce any energy. Therefore, the high-power mode is believed to be an optimal operation condition for the OsMFC with benefits of both desalination and energy recovery.

5.3.3 Membrane orientation
It is known that orientation of FO membrane could affect water flux in an FO process\textsuperscript{89}. In this study, two membrane orientations, the PRO mode and the FO mode, were investigated to understand their effect on the performance of the coupled system. In both orientations, the OsMFC was operated under a high-power mode with an initial salt concentration of 35 g/L (53.5 mS/cm).
The experimental results showed that there was no obvious difference of organic removal between the two conditions, both of which achieved about 85% removal of COD and 6.25% of CE (Fig. 5.4). The organic removal in the OsMFC and the MDC was also similar with both orientations (Table 5.1 and 5.2). The PRO mode produced lightly more electricity than the FO mode. The desalination performance, on the other hand, was clearly different. The FO mode achieved 95.9±0.1 % reduction of conductivity in the final effluent with a salt removal rate of 7.94±0.02 kg/m³/d, significantly higher than 86.7±3.1 % reduction and 5.97±0.63 kg/m³/d in the PRO mode (Fig. 5.4). The final conductivity of the FO and the PRO modes was 2.2±0.1 and 7.1±1.7 mS/cm, respectively (Table 5.2). In contrast to the previous studies that found the PRO orientation generated more water flux than the FO, we found here that the FO mode had more water flux (0.82±0.03 LMH) than the PRO mode (0.63±0.02 LMH) in the OsMFC, resulting in a lower catholyte conductivity than that of the PRO mode (Table 5.1).

![Fig. 5.4 The performance of desalination and COD removal of the coupled system with two membrane orientations in the OsMFC.](image)

At this moment, we do not have a good explanation why the FO mode performed better than the PRO mode, but would like to discuss a possible reason. In the OsMFC, the different in electric
potential between the anode and the cathode could promote the reverse solute flux. Similar to the results of the operation modes, the higher current generation in the PRO mode resulted in more chloride ions transport into the anode, thereby reducing the osmotic pressure. However, that requires further investigation. Furthermore, we are not clear why the PRO mode produced more electricity than the FO mode, and how the electricity production is related to (or affects) the concentration polarization of the membrane. All those issues warrant further research and will be studied in our future work.

5.3.4 Initial salt concentration
To understand the effect of initial salt concentrations (in the catholyte of the OsMFC) on the system performance, three salt concentrations, 10, 35 and 50 g/L, were examined in the coupled system. Similarly to the previous tests, the organic removal was not obviously affected by the initial salt concentration and the system achieved 82-86% of COD removal at three tested salt concentration (Fig. 5.5). The organic removal rates of the OsMFC and the MDC were also similar to those in other testing conditions (Table 5.1 and 5.2). The desalination performance was clearly influenced by the salt concentrations. At 10 g/L, the coupled system achieved almost 100% desalination (99.7±0.0%); the reduction of conductivity decreased to 90.7±0.6% when the initial salt concentration increased to 50 g/L. The water flux was 0.30±0.01 LMH at 10 g/L, much lower than ~0.80 LMH at 35 and 50 g/L (Table 5.1). The conductivity reduction in the OsMFC at 50 g/L was slightly higher than expected: according to dilution estimated from water flux, the estimated conductivity of the cathode effluent from the OsMFC would be about 30 mS/cm, and the actual conductivity was around 28 mS/cm. It is likely that a higher initial salt concentration in the catholyte (draw solution) caused more reverse salt flux. The overall salt
removal rate by the coupled system varied from 2.34±0.00 kg/m$^3$/d at 10 g/L to 9.02±0.36 kg/m$^3$/d at 50 g/L (Fig. 5.5).

![Graph showing COD removal and salt removal rate](image)

Fig. 5.5 The performance of desalination and COD removal of the coupled system at three different initial salt concentrations in the OsMFC.

Table 5.1. Performance parameters of the OsMFC under different operating conditions.

<table>
<thead>
<tr>
<th></th>
<th>PRO (35g/L)</th>
<th>FO-HP (35g/L)</th>
<th>FO-OC (35g/L)</th>
<th>FO-HC (35g/L)</th>
<th>FO (10g/L)</th>
<th>FO (50g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Current (mA)</td>
<td>4.93±0.33</td>
<td>5.06±0.09</td>
<td>N/A</td>
<td>12.92±1.71</td>
<td>3.35±0.25</td>
<td>6.06±0.11</td>
</tr>
<tr>
<td>Catholyte conductivity (mS/cm)</td>
<td>22.1±0.4</td>
<td>20.6±0.3</td>
<td>18.6±1.4</td>
<td>23.3±0.1</td>
<td>10.5±0.1</td>
<td>27.9±0.1</td>
</tr>
<tr>
<td>Water Flux (LMH)</td>
<td>0.63±0.02</td>
<td>0.82±0.02</td>
<td>0.82±0.00</td>
<td>0.63±0.08</td>
<td>0.30±0.01</td>
<td>0.81±0.08</td>
</tr>
<tr>
<td>Anode effluent COD (mg/L)</td>
<td>684.7±56.6</td>
<td>671.0±9.9</td>
<td>743.3±75.7</td>
<td>648.0±11.3</td>
<td>684.0±11.3</td>
<td>688.0±25.4</td>
</tr>
<tr>
<td>COD Removal (%)</td>
<td>23.1±6.4</td>
<td>24.6±1.1</td>
<td>21.2±3.0</td>
<td>27.2±1.3</td>
<td>23.1±1.3</td>
<td>22.7±2.8</td>
</tr>
<tr>
<td>Removal Rate (kg COD/m$^3$/d)</td>
<td>7.2±2.0</td>
<td>7.6±0.3</td>
<td>6.6±0.9</td>
<td>8.4±0.4</td>
<td>7.2±0.4</td>
<td>7.1±0.9</td>
</tr>
</tbody>
</table>

HP: high power; OC: open circuit; HC: high current; N/A: not available.

Table 5.2. Performance parameters of the MDC under different OsMFC operating conditions.

<table>
<thead>
<tr>
<th></th>
<th>PRO (35g/L)</th>
<th>FO-HP (35g/L)</th>
<th>FO-OC (35g/L)</th>
<th>FO-HC (35g/L)</th>
<th>FO (10g/L)</th>
<th>FO (50g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Current (mA)</td>
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<tr>
<td>Catholyte conductivity (mS/cm)</td>
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<tr>
<td>Water Flux (LMH)</td>
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<td></td>
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<tr>
<td>Anode effluent COD (mg/L)</td>
<td></td>
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<td></td>
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<tr>
<td>COD Removal (%)</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Removal Rate (kg COD/m$^3$/d)</td>
<td></td>
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</tbody>
</table>
Those results demonstrated that the coupled system could potentially be used to desalinate waters at different salinities ranging from brackish water, to seawater or some special high-salinity water (e.g., industrial saline wastewater). Although the system had high reduction of conductivity (>90%) at all three salt concentrations, we must understand that salt removal rates are still low because the driving force of desalination is from slow microbial metabolism, suggesting that the potential application of the coupled system can be a pre-desalination process before a conventional desalination process like reverse osmosis or electrodialysis, or a process for desalinating low-salinity water like brackish water. The water flux in the OsMFC was generally lower than that of other FO processes, which might be due to inefficient reactor configuration and low cross-flow velocity of both the anolyte and the catholyte (0.13 cm/s, much lower than 2.5-58 cm/s in other FO studies). However, the OsMFC was still able to increase the amount of saline water by 160% through the FO process, which extracted high-quality water from wastewater (the anolyte) with benefits of reducing the discharge of the treated effluent and improving water reuse. That will help to achieve a sustainable wastewater treatment process with a focus on water reuse and resource recovery from wastewater.
5.3.5 Different catholytes in the MDC

The MDC acted as a real “salt remover” and the post-treatment of wastewater in the coupled system, and its operation was fixed under a high-current mode. The feeding solutions to its anode and the middle (salt) chambers came from the OsMFC, but its catholyte was independent from the OsMFC. In this study, we used the acidified water as the cathode, which was proven effective and low cost (3% of the phosphate buffer solution that is commonly used in bioelectrochemical systems) however, it is still of great interest to explore alternative catholytes, because the acidified water could increase the operating cost. Therefore, we examined two other possible catholytes: salt solution (35 g NaCl/L) and the MDC anode effluent. In this test, the organic concentration in the feeding solution to the OsMFC was reduced to 0.5 g/L sodium acetate; because our previous results showed that the anode effluent from the MDC still contained more than 120 mg/L (Table 5.2). If this effluent is used as the catholyte of the MDC, it could decrease the electricity generation by stimulating the growth of heterotrophic bacteria.53

The OsMFC performance was not affected by the different MDC catholyte, while the MDC performance obviously varied. The acidified water resulted in the highest current generation (52.9±2.1 mA), followed by the salt solution (35.9±4.2 mA) and the anode effluent (27.4±1.3 mA), as shown in Figure 5.6. Some instability in current generation was observed due to electrode connection, temperature variation, or other unknown factors. The acidified water also achieved the best desalination performance among the three, with a final conductivity of 5.4±0.7 mS/cm and a salt removal rate of 5.98±0.34 kg/m³/d, because of its high current production.
However, the higher current generation with the salt solution did not lead to better desalination than the anode effluent.

The MDC with the salt solution as a catholyte produced a final conductivity of 16.9±0.3 mS/cm with a salt removal rate of 1.56±0.22 kg/m³/d; while the catholyte using the anode effluent resulted in a final conductivity of 13.0±0.7 mS/cm and a salt removal rate of 2.75±0.69 kg/m³/d. Desalination with the salt-solution catholyte was lower because the salinity of the catholyte was higher than of the desalinated water in the middle chamber, and a salt gradient across the CEM prevented the transport of sodium ions from the middle chamber to the cathode; electricity generation was not affected by this phenomenon, because the sodium ions in the catholyte could move into the middle chamber. This result indicated that, although seawater is a low-cost catholyte for MDCs ⁴⁸, its high salt contents will negatively affect desalination. The catholyte using the anode effluent will potentially have biofouling issues, which require a long-term examination of its stability. The acidified water is promising because of its superior performance, and its economics could be justified by comparing the operating cost and economic benefits from better desalination when MDCs are scaled up to a pilot system (economic analysis of a bench-scale system is not very informative).
Fig. 5.6 Current generation in the MDC with three different catholytes (acidified water—black color, salt solution—red color, and anode effluent—green color).

5.4. Conclusions
This study has demonstrated the feasibility of a membrane-based bioelectrochemical system that can be potentially used for simultaneous wastewater treatment and water desalination. By hydraulically linking an OsMFC to an MDC, the system significantly improved desalination and organic removal compared with an MDC. Investigating several important factors, such as operation modes, membrane orientation, initial salt concentrations and catholytes, improved our understanding of the coupled system operation. To further develop this system towards practical application, we must address challenges like system scale-up, FO membrane fouling, reduced energy consumption (e.g., reducing aeration in OsMFCs), and the electric linkage between OsMFCs and MDCs.
Acknowledgement

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Chapter 6 Synthesizing Nitrogen-doped Activated Carbon as a Highly Active Catalyst and Probing its Active Sites for Oxygen Reduction Reaction for Microbial Fuel Cells

Abstract

Cost-effective cathode catalysts are critical to the development of microbial fuel cell (MFC) technology. Herein, a synthesis route is presented to control the nitrogen content and nitrogen functionalities in the nitrogen-doped activated carbon (AC) as a low cost and efficient catalyst for oxygen reduction reaction (ORR). It was demonstrated that the keys to successful nitrogen doping were the proper pretreatment with acid and alkaline consecutively and the use of a solid state nitrogen precursor. The AC pretreated with both acidic and alkaline solutions resulted in a nitrogen concentration of 8.65% (atom %) (in which 5.56 % is pyridinic-N) on its surface, and exhibited an outstanding electrocatalytic performance for ORR in electrochemistry test and MFC test. A good agreement between pyridinic-N content and ORR catalytic activity was observed, indicating that pyridinic-N might be the most active site of ORR in the nitrogen-doped AC. The pretreated nitrogen-doped AC catalysts resulted in a higher maximum power density than the untreated AC and the commercial Pt/C (10% Pt) catalysts. The outstanding performance associated with the advantages such as simple and convenient preparing procedure, easily obtained raw materials, and low cost, make the pretreated nitrogen-doped AC promising in the ongoing effort to scale up MFCs.
6.1 Introduction
Microbial fuel cells (MFCs) have been intensively studied as a sustainable wastewater treatment technology. In an MFC, the electrochemically active bacteria grown on an anode electrode oxidize organic matters in wastewater and release the electrons to the anode electrode; the released electrons then travel through an external circuit to reduce the terminal electron acceptors in the cathode. With recovering energy from organic wastes, MFCs have a potential to become an energy-neutral (even positive) treatment process. The terminal electron acceptors in the cathode play a critical role in both organic oxidation and energy recovery. Oxygen is the most commonly used terminal electron acceptor and considered to be suitable for MFC application because of its high reduction potential and readily availability. However, due to the high energy barrier of oxygen reduction reaction (ORR), a catalyst will be needed to facilitate the cathode reaction in an MFC. Currently, the Pt-based catalysts are the most widely applied cathode catalyst in the laboratory MFC system, which makes the capital cost of MFC technology prohibitively high for a practical application. Therefore, exploring a low-cost and efficient alternative ORR catalyst to the Pt-based materials is of great importance to bring the MFC technology into a practical scale. Some alternative ORR catalysts have been studied in MFCs including transition metal complexes, metal oxides, nitrogen-doped carbon nanotubes, and graphenes, and microorganisms. However, the limitations associated with these alternatives, such as high manufacturing cost, complex preparing procedure, poor durability and low performance, prevent them from being an ideal candidate for large scale MFC applications.

Activated carbon (AC) is a common carbon material that can be facilely and economically produced from various carbonaceous sources such as wood, nutshells, coconut husk, peat,
lignite, coal, and petroleum pitch\textsuperscript{102}. Recently, AC was demonstrated as an alternative cathode catalyst to Pt in several MFCs\textsuperscript{102-106}, in which the AC based cathode electrodes achieved relatively higher power densities compared with the non-catalyzed cathodes; a long term study showed that the AC cathodes exhibited much better durability than the Pt/C based cathode\textsuperscript{107}. In addition, AC has a large surface area in excess of 500 m\textsuperscript{2} g\textsuperscript{-1} and its low cost is very attractive compared with other nanostructured carbon materials (e.g. carbon nanotubes, or graphene) or the Pt-based catalysts, thereby making AC a very promising catalyst for large scale MFCs.

However, the low catalytic activity for ORR in AC has greatly limited its widespread use in MFCs. It was recognized that proper modification of AC may greatly affect its catalytic performance, and among the modifying methods, nitrogen doping on some nanostructured carbon has been demonstrated to be an effective strategy to improve ORR catalytic performance\textsuperscript{108-109}. Actually, there have also been some attempts to improve the ORR catalytic performance of AC through nitrogen doping\textsuperscript{104,110-111}. These nitrogen-doped AC materials, though somehow achieving enhanced ORR activity, still cannot satisfy the MFCs application most likely due to the low nitrogen content (typically below 2\%). The recent research found that three types of typical doped nitrogen, i.e. pyridinic-N, pyrrolic-N, and quaternary-N, could make different contributions to improving ORR activity: the pyridinic-N and the pyrrolic-N could reduce the thermodynamic barrier of ORR, while the quaternary-N could enhance the kinetic performance of ORR\textsuperscript{112}. Nitrogen doped carbon nanostructures indicated that increasing the contents of the pyridinic-N and the pyrrolic-N seemed to be more important since both can be beneficial to reducing the energy barrier of ORR\textsuperscript{113}. 
Those prior findings and the strong need for cost effective cathode catalysts for large-scale MFC development inspire us to explore a proper nitrogen doping strategy for improving AC catalysts. We hypothesize that the ORR catalytic activity of the nitrogen-doped AC would benefit from 1) increasing nitrogen content; and 2) a reasonable control of N functionality. In this study, we have developed an effective and reliable method to prepare the nitrogen-doped AC with controllability in both total N-doped content and N-functionalities. We have conducted a series of experiments to examine the effects of the pretreatment on the nitrogen-doped AC, and two keys were demonstrated to be very important in fabricating an ideal nitrogen-doped AC based cathode catalyst that could outperform Pt/C catalysts for the MFC application: 1) pretreatment of AC with acidic or alkaline solutions successively before the nitrogen-doping reaction, and 2) use a solid nitrogen source, i.e. cyanamide.

6.2 Methods and materials

6.2.1 Synthesis of the AC catalysts
The nitrogen-doped AC was synthesized by using commercially available activated carbon (Fisher Scientific, Bridgewater, NJ, USA), and three different types of the nitrogen-doped AC were prepared: 1) direct nitrogen-doped AC (AC_N) without any pretreatment; 2) acid pretreated nitrogen-doped AC (Acidic-AC_N); and 3) acid and alkaline pretreated nitrogen-doped AC (Acidic/Basic-AC_N). During the synthesis of the Acidic-AC_N and the Acidic/Basic-AC_N, the acidic pretreatment process was performed as the following: 2 grams of AC powder was added into a solution containing 25 mL of H_2SO_4 (98 %) and 2 grams of KMnO_4 and mixed for 3 hours. Afterwards, the acid treated AC was washed thoroughly using DI water, and then used for nitrogen doping. To prepare the Acidic/Basic-AC_N, the acid pretreated AC was further treated...
in a 3 M KOH solution at 180 °C for 10 hours; the acidic-basic pretreated AC was then thoroughly washed with DI water and used in the following nitrogen doping.

The nitrogen precursor used in this study was cyanamide (Sigma-Aldrich, St. Louis, MO, USA). The AC samples and cyanamide were added in a 1:5 ratio (mass) and well mixed before they were loaded into a programmable tube furnace (Lindberg, Thermo Scientific, USA). Before the doping, the tube furnace was flushed with Argon for 10 min. The temperature was increased from the room temperature to 80 °C in 10 min and maintained at 80 °C for one hour; then the temperature was further increased to 750 °C in 4 hr and maintained at 750 °C for additional 2 hr. During the entire doping period, the tube was flushed with argon gas at a flow rate of 0.1 mL s⁻¹.

Fig. 6.1. Schematic illustration for fabricating the Acidic/Basic-ACN.
6.2.2 Characterization of the AC catalysts
The morphology of the nitrogen-doped AC was characterized by scanning electron microscope (SEM) (Hitachi S-4800). Brunauer-Emmett-Teller (BET) test was conducted to examine the surface area and pore size distribution of the catalysts (ASAP 2020, Micromeritics, Norcross, GA, USA). During the BET test, the samples were first degased and then used to adsorb N\textsubscript{2} at 76 K. The micropore area and volume was calculated by using t-plot method. XPS (5950A ESCA Spectrometer, H.P.) was employed to study the surface chemistry composition of the catalysts, and to compare the nitrogen content between different nitrogen-doped AC catalysts; the spectra were scanned from 0 eV to 1000 eV, and were analyzed using XPSPEAK 4.1.

Linear Sweep Voltammetry (LSV) was used to examine the electrochemical performance of the AC catalysts. The catalyst ink was prepared by dissolving 5 mg of the catalyst in 0.5 mL of 0.5% Nafion solution (Sigma-Aldrich, St. Louis, MO, USA). The ink was vortexed for 5 min and then ultrasonicated for 30 min to ensure well dispersion of the catalyst. After ultrasonication, 6 µL of the ink was pipetted to the top of a glassy carbon electrode, which was dried in the air and then used in the electrochemical test. During the LSV test, the working electrode was mounted on a rotating disk electrode (RRDE-3A, BASi, West Lafayette, IN, USA). To calculate the number of electrons transferred during ORR as previously described \textsuperscript{114}, the rotating speed of the electrode was varied from 100 to 3600 rpm. The counter electrode was a Pt wire (CHI115, CH Instruments, Austin, TX, USA), and the reference electrode was Ag/AgCl (Saturated KCl, 0.197 V vs. standard hydrogen electrode). The potentials reported in the LSV test were the values vs. Ag/AgCl reference electrode unless noted otherwise. The electrolyte used in the LSV tests was 100 mM phosphate buffer solution containing (per Liter): K\textsubscript{2}HPO\textsubscript{4}, 10.7 g; and KH\textsubscript{2}PO\textsubscript{4}, 5.3 g.
Before the LSV test started, the electrolyte was aerated with oxygen for 30 min, and the aeration was continued at the head space throughout the LSV test. The voltage was scanned from 0.8 to -0.8 V at a scan rate of 5 mV s\(^{-1}\) using a potentiostat (600E, CH Instruments, Austin, TX USA).

6.2.3 MFC test
The MFC test was conducted in an H-shape reactor. The anode electrode was a 5-cm long carbon brush. The anolyte contained (per liter of tap water): sodium acetate, 1 g; NH\(_4\)Cl, 0.15 g; NaCl, 0.5 g; MgSO\(_4\), 0.015 g; CaCl\(_2\), 0.02 g; KH\(_2\)PO\(_4\), 0.53 g; K\(_2\)HPO\(_4\), 1.07 g; yeast extract, 0.1 g; and trace element, 1 mL\(^{51}\). The cathode electrode was carbon cloth coated with the prepared AC catalysts. The catholyte was 100 mM phosphate buffer solution. The anode chamber and cathode chamber were separated by a cation exchange membrane (Membrane International, Inc., Ringwood, NJ, USA). The anode chamber was inoculated with digester effluent from South Shore Wastewater Treatment Plant (Milwaukee, WI, USA). The cathode chamber was aerated with air with a flow rate of 50 mL min\(^{-1}\). Both the anolyte and the catholyte were mixed using stirring bars.

Five different cathode catalysts were tested, including AC, AC\(_N\), Acidic-AC\(_N\), Acidic/Basic-AC\(_N\) and Pt/C (10% Pt, Fuel Cell Earth, Stoneham, MA, USA). Each catalyst was loaded onto a piece of carbon cloth using 0.5% Nafion solution (Sigma-Aldrich, St. Louis, MO, USA) as binder with a loading rate of 5 mg cm\(^{-2}\). The dimension of each carbon cloth was 1 cm by 3 cm. Prior to being coated, the carbon cloth was soaked in acetone overnight and then heat treated under 350\(^{\circ}\)C for one hour.
The MFC performance was monitored and examined by using polarization tests and current generation across an external resistor. The polarization test was conducted by using a potentiostat (Reference 600, Gamry Instruments, Warminster, PA, USA) at a scan rate of 0.1 mV s\(^{-1}\): the cathode electrode functioned as a working electrode, and the anode electrode acted as both the counter and reference electrodes. The polarization test was duplicated for each catalyst. Four AC based catalysts, AC, AC\(_N\), Acidic-AC\(_N\) and Acidic/Basic-AC\(_N\), were compared for their current profile across the external resistance of 33 Ω in a batch operation. To do this, four cathodes loaded with different AC catalysts were simultaneously connected to the common anode electrode (so that the influence of different anode electrode would be minimized) in an MFC. One batch operation last for 24 hr, and the anolyte and catholyte were replaced with the fresh medium after each batch.

### 6.3 Results

#### 6.3.1 Synthesis and characterization of the AC Catalysts

The entire procedure for preparing the Acidic/Basic-AC\(_N\) was demonstrated in Fig. 1. The synthesis starts from treatment of AC with strong oxidizing acid, i.e. concentrated H\(_2\)SO\(_4\) with KMnO\(_4\), which produces a large amount oxygen-rich group; the following KOH treatment then leads to the activation of AC\(^{115}\); after introducing N source (cyanamide), the oxygen-rich groups in AC would react with amine groups in NH\(_2\)CN to form a layer of C\(_3\)N\(_4\) polymer covered on AC; the final calcination at 750 °C leads to the nitrogen-doped AC products through N-doping reaction between AC and the produced gas (e. g., C\(_2\)N\(_2\)^+\(^\_\), C\(_3\)N\(_2\)^+\(^\_\), NH\(_3\)) from decomposition of C\(_3\)N\(_4\)\(^{116}\).
The representative SEM images of all AC samples are shown in two scales in Fig. 2, from which one can observe there is no significant difference in morphology among these samples, indicating that neither the acidic/basic pretreatment nor the nitrogen doping reaction obviously affect the morphology of the catalysts. This suggests that the morphology may not play a key role in impacting the performance of those AC catalysts studied here. The Acidic/Basic-AC\textsubscript{N} was further characterized by taking element mapping images of carbon and nitrogen (Fig. 3a-c), in which the green dots (Fig.3b) and the yellow dots (Fig.3c) are attributed to carbon and nitrogen elements, respectively. One can observe that the nitrogen elements were uniformly dispersed on the Acidic/Basic-AC\textsubscript{N} sample, demonstrating the N can be uniformly doped in carbon by using the present method. Although the nitrogen-doped AC catalysts had smaller surface areas and micropore areas than the plain AC material (Table 1), their ORR catalytic performances had been improved remarkably (more details in the following sections), indicating that the surface area had little contribution to the improvement in ORR catalytic activity of the nitrogen-doped ACs.

Fig. 6.2 SEM images of the AC (a, b), the AC\textsubscript{N} (c, d), the Acidic-AC\textsubscript{N} (e, f), and the Acidic/Basic-AC\textsubscript{N} (g, h).
Fig. 6.3. Zero-energy loss bright field image of the Acidic/Basic- \( \text{AC}_N \) (a), the corresponding carbon element mapping (b), and the nitrogen element mapping (c).

The XPS spectra of the \( \text{AC}_N \), the Acidic-\( \text{AC}_N \) and the Acidic/Basic-\( \text{AC}_N \) catalysts are presented in Fig. 4. According to the XPS spectra, the nitrogen contents of the three catalysts are: 4.2% for the \( \text{AC}_N \), 6.0% for the Acidic-\( \text{AC}_N \) and 8.7% for the Acidic/Basic-\( \text{AC}_N \), significantly higher than those (around 2%) in two prior studies of the nitrogen-doped activated carbon \(^{104}\) and nitrogen-doped carbon black \(^{110}\) as a cathode catalyst in MFCs. The acidic pretreatment increased the nitrogen content by 45% (the \( \text{AC}_N \) vs. the Acidic-\( \text{AC}_N \)), and the combined acidic and basic pretreatment further improved the nitrogen content by another 45% (the Acidic-\( \text{AC}_N \) vs. the Acidic/Basic-\( \text{AC}_N \)), which doubled the nitrogen content compared with the \( \text{AC}_N \), indicating that pretreatment is a key factor in preparing the nitrogen-doped ACs.
6.3.2 LSV Test
The results of the LSV tests of the AC, the AC$_N$, the Acidic-AC$_N$, the Acidic/Basic-AC$_N$ and the Pt/C are presented in Fig. 5, and confirmed our hypothesis that nitrogen doping could increase the ORR catalytic performances of AC and that different pretreatment methods would result in the materials with different catalytic performance. According to the LSV, the AC had the most negative ORR onset potential, which is about 60 mV; while, as expected, the Pt/C showed the most positive ORR onset potential of +300 mV. Direct nitrogen doping (AC$_N$) did not change the onset potential; however, the current density of AC$_N$ was higher than that of AC, likely because of the increased quaternary-N content. On the other hand, noticeable positive shifts in ORR onset potential were observed in the pretreated nitrogen-doped AC: the Acidic-AC$_N$ had an onset
potential of 160 mV while the Acidic/Basic-AC_N exhibited an onset potential of 180 mV. Comparing with the AC_N, these onset potentials mark improvements of +100 mV and +120 mV, respectively, likely because of the increased pyridinic-N content resulted from pretreatment.

The pretreated nitrogen-doped AC also showed higher current densities in LSV, which confirmed the importance of proper pretreatment. In more details, the AC_N reached a limiting current density of 4.67 mA·cm^{-2}, which was 33% higher than that of the raw AC (3.51 mA·cm^{-2}). The limiting current densities of the Acidic/Basic-AC_N and the Acidic-AC_N were 7.18 mA·cm^{-2} and 5.89 mA·cm^{-2}, respectively. The current densities of the tested catalysts generally follow a trend of the AC < the AC_N < the Acidic-AC_N < the Acidic/Basic-AC_N. The current density of the Acidic/Basic-AC_N was comparable to that of the Pt/C. To our best knowledge, no previous studies have reported the AC or the AC based catalysts with similar current densities to the Pt/C in an ORR. According to the calculated number of electrons transferred during ORR (Table 2),
the ORR prefers to take place in a 4e⁻ transfer pathway when using the pretreated nitrogen doped ACs as catalysts. The raw AC had a calculated electron transfer number of 2.61, similar to that of the ACₙ. A electron transfer number close to 2 indicates that the ORR was possibly proceeded in a 2e⁻ transfer pathway, which was less favorable in an MFC cathode \(^{117}\).

**6.3.3 MFC Performance**

The AC catalysts were examined in an MFC for power production and current generation. The maximum power densities of the MFC with different cathode catalysts obtained from polarization tests are presented in Fig. 6. The Acidic-ACₙ and the Acidic/Basic-ACₙ cathodes resulted in a maximum power density of 0.58±0.04 W m\(^{-2}\) and 0.65±0.02 W m\(^{-2}\) (based on projected cathode area), respectively, 1.4 or 1.6 times higher than that of the ACₙ (0.41±0.00 W m\(^{-2}\)). For comparison, the MFC with the Pt/C cathode reached a maximum power density of 0.45±0.04 W m\(^{-2}\), while the raw AC cathode had a maximum power density of 0.31±0.08 W m\(^{-2}\). The batch current profiles for the AC cathodes were compared in Fig.7. All three nitrogen-doped AC cathodes exhibited higher current than the non-doped AC cathode. The direct doped ACₙ only showed a moderate improvement comparing to the AC; however, the pretreated nitrogen-doped AC achieved the currents roughly 4 times higher than that of the ACₙ and 5 times higher than that of the raw AC.
6.4 Discussions

The successful doping of AC in this study relied on two key factors: 1) proper pretreatment, and 2) the decomposition of solid precursor as a nitrogen source. The well-ordered structure of AC makes it hard for nitrogen atom to be doped into the carbon matrix; thus, it is important to
introduce defects onto the surface of the carbon. The present method, through pretreatment of AC with acid and alkaline solution successively, was supposed to introduce a large amount of defects on the surface of AC. These introduced defects then became the active sites for nitrogen doping in following steps. A solid nitrogen precursor (e.g. cyanamide) rather than conventional NH₃ gas was used in this study, which allowed the nitrogen precursor to be in a sufficient contact with the AC surface or even to be seeped in the porous channel of AC, and the in situ produced nitrogen-sources thus could be uniformly and efficiently doped in AC upon annealing. Such a designed process could also increase the pyridinic-N and pyrrolic-N content in AC. 112

Table 6.1 The surface area and micropore area of the different materials.

<table>
<thead>
<tr>
<th></th>
<th>AC</th>
<th>Acidic-AC</th>
<th>ACN</th>
<th>Acidic-ACN</th>
<th>Acidic/Basic-AC</th>
<th>Acidic/Basic-ACN</th>
<th>Pt/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET Surface Area</td>
<td>861.68</td>
<td>693.49</td>
<td>687.19</td>
<td>679.91</td>
<td>634.64</td>
<td>672.43</td>
<td>208.36</td>
</tr>
<tr>
<td>Area (m² g⁻¹)</td>
<td>521.78</td>
<td>401.61</td>
<td>390.60</td>
<td>391.35</td>
<td>357.89</td>
<td>398.92</td>
<td>67.79</td>
</tr>
<tr>
<td>Micropore Area</td>
<td>521.78</td>
<td>401.61</td>
<td>390.60</td>
<td>391.35</td>
<td>357.89</td>
<td>398.92</td>
<td>67.79</td>
</tr>
</tbody>
</table>

The deconvoluted N 1s spectra of three nitrogen-doped AC showed distinct differences in terms of N functionalities. The relative pyridinic-N percentage (Table 2) increased as acid and alkaline pretreatments were employed and became dominant in Acidic/Basic-ACN. Along with the increased pyridinic-N content, the catalytic activity of nitrogen doped AC increased as well. In terms of thermodynamics, the ORR onset potential shifted positively with pretreatments. The limiting current density in LSV, which was an indicator of kinetic property, also showed that the pretreated nitrogen-doped AC had higher current densities than direct doped AC. The agreements were good between the pyridinic-N content and increased ORR catalytic performance.
of nitrogen doped AC; however, such agreements were not found for the pyrrolic-N or quaternary-N (Fig. S3, Supporting Information). These results suggested that the pyridinic-N might be the most active site for ORR in nitrogen-doped AC; however, the contribution of pyrrolic-N or quaternary-N should not be excluded based on these results.

Table 6.2 The results of the XPS tests of three nitrogen-doped AC catalysts.

<table>
<thead>
<tr>
<th></th>
<th>Total surface N content (atom %)</th>
<th>Surface content of different N functionalities (atom %)</th>
<th>Number of e⁻ transferred in ORR</th>
<th>The ORR onset potential (mV)</th>
<th>I_{lim} in LSV (mA cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pyridinic</td>
<td>Pyrrolic</td>
<td>Quaternary</td>
<td></td>
</tr>
<tr>
<td>AC_N</td>
<td>4.20</td>
<td>1.46 (35%)</td>
<td>1.48 (35%)</td>
<td>1.25 (30%)</td>
<td>2.39</td>
</tr>
<tr>
<td>Acidic-AC_N</td>
<td>6.00</td>
<td>2.30 (38%)</td>
<td>1.87 (31%)</td>
<td>1.83 (31%)</td>
<td>4.09</td>
</tr>
<tr>
<td>Acidic/Basic-AC_N</td>
<td>8.65</td>
<td>5.56 (64%)</td>
<td>1.36 (16%)</td>
<td>1.73 (20%)</td>
<td>3.99</td>
</tr>
</tbody>
</table>

* the relative percentage of each N functionality among the N content on AC surface

In the MFC test, the nitrogen-doped AC with a higher pyridinic-N content showed higher power densities and current densities. More remarkably, the Acidic-AC_N and Acidic/Basic-AC_N resulted in power densities even higher than Pt/C. Considering that the morphology and surface area were not significantly altered by pretreatment and nitrogen doping, the superior performances of the Acidic-AC_N and the Acidic/Basic-AC_N should be attributed to the increased nitrogen content (especially the pyridinic-N) as a result of proper synthesis route. This result emphasized the importance of proper pretreatment and nitrogen precursor selection in terms of improving the ORR catalytic performances of the AC for MFC cathode. The doping route employed in the current study enabled us to control the nitrogen content and specific nitrogen moieties. Although recent studies have confirmed that the pyridinic-N and the pyrrolic-N
contribute mostly to the enhanced ORR catalytic activity of nitrogen doped nano structures\textsuperscript{113}, our study suggested that the pyridinic-N is probably the most active site for ORR with the nitrogen-doped AC.

The doping method presented in this work can easily be adopted for producing a large quantity of the nitrogen-doped AC catalysts. We estimated the costs of the nitrogen-doped AC (more details in Supporting Information) as $6.40 \text{ g}^{-1}$, of which 91.3\% was attributed to cyanamide. Thus, to further reduce the catalyst cost, cyanamide must be replaced with other low-cost nitrogen precursors such as melamine and urine. Even using cyanamide, the cost of the Acidic/Basic- AC\textsubscript{N} was about 10\% of the Pt/C powder. In addition to the cost advantages, the nitrogen-doped AC or AC catalyst showed better long term stability than the Pt/C cathode and less susceptible to sulfide\textsuperscript{118}. These features will make it more advantageous to use AC-based catalysts for large-scale MFC development.

The above results clearly demonstrate that the proper doping method is very critical to tune the N-group functionality that is of vital importance to affect the ORR catalytic activity. The as-developed Acidic/Basic-AC\textsubscript{N} exhibits significantly enhanced catalytic activity for ORR in comparison with raw AC. More importantly, when using as cathode materials of MFC, the as-developed Acidic/Basic-AC\textsubscript{N} can thoroughly defeat the well-known Pt/C catalysts in terms of the most important performance parameter of MFC, i.e. power density. The outstanding properties could be reasonably attributed to high pyridine-N doping content, and large surface area (twice higher than Pt/C) in Acidic/Basic-AC\textsubscript{N}. More importantly, the Acidic/Basic-AC\textsubscript{N} can be
conveniently, effectively, and economically prepared at a high yield (more than 80% relative to AC), which makes it possible to large-scale produce cost-effective and high-activity cathode catalysts for practical MFC application.
Chapter 7 Conclusions

The sustainable desalination using BES is investigated in this thesis. Experimental proofs have been given that using the BES will reduce the energy consumption and time required for desalination. By incorporating forward osmosis technology into BES, water reclamation could be achieved simultaneously. However, due to the high rejection rate of ions by forward osmosis membrane, directly using forward osmosis in microbial desalination cell may not result in the best performance. Alternatively, by using two separate reactors for water reclamation and desalination could result in better desalination, although this comes at the cost of building another reactor. We have shown that the cost of BES could be reduced by replacing the Pt catalyst in cathode with cost efficient AC based catalyst. The using of AC based catalyst while still achieving a power density higher than that using Pt cathode makes the BES closer to full scale application.

Since the desalination process is relatively slow in MDC, it is better to use it as a pretreatment desalination system to lower the downstream energy demand and cost. We have gained a lot of knowledge of lab scale MDC and focus of research now should be shifted to study pilot scale or even full scale MDC. Considering that stacked configuration allows higher desalination efficiency per electron transferred, it is important to study the pilot scale stacked MDC for desalination. By using the AC based cathode, the cost of such system could be greatly reduced.
References


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Appendix 1

UMDC set up
The UMDC was constructed as a tubular bioreactor with two compartments (the anode and salt chamber). Carbon brushes were used as the anode electrode materials. The UMDC consisted of one anode tube made of anion exchange membrane (AEM, AMI-7001, Membrane International, Inc., Glen Rock, NJ) within a larger cation exchange membrane tube (CEM, CMI-7000, Membrane International, Inc.). The diameters of the AEM and CEM tubes were 6 cm and 7 cm, respectively, and the effective lengths of both tubes were ~ 70 cm, resulting in an anode liquid volume of 1.9 L (excluding the anode electrode) and a saline water volume of 0.85 L.

![Diagram of UMDC](image)

The above schematic of the UMDC was adopted from Jacobson, K.S., Drew, D. and He, Z. (2011) Use of a liter-scale upflow microbial desalination cell as a platform to study bioelectrochemical desalination with salt solution or artificial seawater. Environmental Science & Technology. Vol 45, pp 4652-4657.

Calculation of the energy stored in an ultracapacitor
When an ultracapacitor was charged from V_d (discharging voltage, close to zero) to V_c (charging voltage), the energy (E_c) stored in the capacitor was calculated as:

\[ E_c = 0.5 \times C \times (V_c^2 - V_d^2) \]
Fig. S1.1. Polarization curves of the UMDC system in serial and parallel connections.
Fig. S1.2. The conductivity of the salt effluents from the UMDC system in parallel connection and the energy consumption by the ED for desalinating those effluents. The salt solution was fed in batch during the 18-h testing period.

Fig. S1.3. Current generation of the UMDC system in parallel connection. The salt solution was fed as batch during the 18-h testing period.
Fig. S1.4. The pH of the effluent from the anode and salt chambers of the UMDC system: (A) in serial connection and (B) in parallel connection. The salt solution was fed in batch during the 18-h testing period.
Appendix 2

Materials and Methods

OsMDC setup and operation

Both OsMDC and MDC were made of glass reactors with three chambers, anode, middle and cathode. In the conventional MDC, an anion exchange membrane (AEM, Membrane International Inc., Ringwood, NJ, USA) was installed between the anode and the middle chamber; in the OsMDC, the AEM was replaced by an FO membrane (Hydration Technology Innovations, LLC, Albany, OR, USA). The cathode and the middle chambers were separated by a cation exchange membrane (Membrane International Inc.) in both MDCs. The liquid volumes of the anode and the cathode chambers were ~ 60 mL each. The middle chamber contained 25 mL of saline water. Both the anode electrode and cathode electrode were carbon brush (Gordon Brush Mfg. Co., Inc., Commerce, CA, USA). Before use, the brush electrodes were pre-treated by immersion in acetone overnight and heated at 450 °C for 30 min.

The OsMDC and MDC were operated under a room temperature of ~ 20 °C. The anode was continuously fed at a hydraulic retention time (HRT) of 6 hours. The anode feeding solution (artificial wastewater) was prepared containing (per L of tap water): sodium acetate, 4 g; NH₄Cl, 0.15 g; NaCl, 0.5 g; MgSO₄, 0.015 g; CaCl₂, 0.02 g; NaHCO₃, 0.1 g; KH₂PO₄, 0.53 g; K₂HPO₄, 1.07 g; and trace element, 1 mL. The cathode was continuously fed with (per L of tap water): K₃Fe(CN)₆, 32.926g, KH₂PO₄, 5.3 g and K₂HPO₄, 10.7 g. The flow rates of anolyte and catholyte were both 0.17 mL per min, resulting in a hydraulic retention time of 5.9 h in each chamber. The anolyte was recirculated at 30 mL/min. The saline water was prepared by dissolving either NaCl
(5, 10 or 20 g/L) or aquarium sea salt (35 g/L. Aquarium Systems, Inc., Mentor, OH, USA) in tap water. The middle chamber was operated as the fed-batch with a cycle of three days and the saline water was recirculated at 15 mL/min.

**Measurement and Analysis**

The cell voltage was recorded every 180 seconds by a digital multimeter (2700, Keithley Instruments, Inc., Cleveland, OH, USA). The pH was measured using a benchtop pH meter (Oakton Instruments, Vernon Hills, IL, USA). The conductivity was measured by a benchtop conductivity meter (Mettler-Toledo, Columbus, OH, USA). The power density and current density were calculated based on the anode liquid volume. Water flux into the middle chamber was measured by using digital scales for the change of water weight during the course of experiments. Water flux was either expressed in mL or calculated as liter per surface area of the membrane per hour (L m⁻² h⁻¹ - LMH). The electrochemical impedance spectra of the membranes were collected in a four-electrode system using a potentiostat (Gamry Instruments, Warminster, PA, USA).
Fig. S2.1. The conductivities of the saline water (initial concentration of 10 g/L) from the actual measurement and the estimation with dilution effect only.
Fig. S2.2 Current generation in the OsMDC treating 10 g NaCl/L saline water in an operating cycle of three days.

The external resistance was 1 Ω.
Fig. S2.3. The Bode plots of the membrane impedance measured by electrochemical impedance spectroscopy.
Appendix 3

Fig. S3.1. The whole XPS spectrum of a) ACₙ, b) Acidic-ACₙ and c) Acidic/Basic-ACₙ. The corresponding peaks are labeled.
Fig. S3.2. The LSV of a) AC, b) AC_N, c) Acidic-AC_N, d) Acidic/Basic-AC_N and e) Pt/C at different rotation speeds.
Fig. S3.3. Koutecky-Levich Plot of a) AC, b) ACN, c) Acidic-ACN, d) Acidic/Basic-ACN and e) Pt/C (current densities were picked at -150 mV vs. Ag/AgCl electrode).
Fig. S3.4. Current densities of the Pt/C and the Acidic/Basic-\textit{AC}_N electrodes during the chronoamperometry test.
Fig. S3.5. The correlations between different N functionalities and ORR catalytic activity a) Pyridinic-N, b) Pyrrolic-N and c) quaternary-N.
Table S3.1. The surface area and micropore area of the different materials.

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<td>357.89</td>
<td>398.92</td>
<td>67.79</td>
</tr>
</tbody>
</table>

Table S3.2. The ratio of different atom in the nitrogen-doped AC

<table>
<thead>
<tr>
<th></th>
<th>ACN</th>
<th>Acidic-ACN</th>
<th>Acidic/Basic-ACN</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.849</td>
<td>0.821</td>
<td>0.828</td>
</tr>
<tr>
<td>N</td>
<td>0.042</td>
<td>0.060</td>
<td>0.087</td>
</tr>
<tr>
<td>O</td>
<td>0.109</td>
<td>0.119</td>
<td>0.085</td>
</tr>
</tbody>
</table>
Curriculum Vitae

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Place of Birth: Beijing, China

Education:

Master of Science in Engineering, Clarkson University, 2010

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