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Membranes for bioelectrochemical systems: challenges and research advances

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Membranes for bioelectrochemical systems: challenges and research advances

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Increasing energy demand has been a big challenge for current society, as the fossil fuel sources are gradually decreasing. Hence, development of renewable and sustainable energy sources for the future is considered one of the top priorities in national strategic plans. Bioenergy can meet future energy requirements – renewability, sustainability, and even carbon-neutrality. Bioenergy production from wastes and wastewaters is especially attractive because of dual benefits of energy generation and contaminant stabilization. There are several bioenergy technologies using wastes and wastewaters as electron donor, which include anaerobic digestion, dark biohydrogen fermentation, biohydrogen production using photosynthetic microorganisms, and bioelectrochemical systems (BESs). Among them BES seems to be very promising as we can produce a variety of value-added products from wastes and wastewaters, such as electric power, hydrogen gas, hydrogen peroxide, acetate, ethanol etc. Most of the traditional BES uses a membrane to separate the anode and cathode chamber, which is essential for improving microbial metabolism on the anode and the recovery of value-added products on the cathode. Performance of BES lacking a membrane can be seriously deteriorated, due to oxygen diffusion or substantial loss of synthesized products. For this reason, usage of a membrane seems essential to facilitate BES performance. However, a membrane can bring several technical challenges to BES application compared to membrane-less BES. These challenges include poor proton permeability, substrate loss, oxygen back diffusion, pH gradient, internal resistance, biofouling, etc. This paper aims to review the major technical barriers associated with membranes and future research directions for their application in BESs.

Keywords: bioelectrochemical system; membrane; bioenergy; renewable energy; value-added products

1. Introduction

Bioelectrochemical system (BES) is a promising technology for bioenergy (e.g. bioelectricity, biohydrogen) and value-added products (e.g. acetate, hydrogen peroxide) recovery from organic waste and wastewaters.[1–7] New microbiological physiology, versatile application, and substantial market potential of BES have attracted many scientists and engineers.[1,2] BES can simultaneously treat organic wastewater with 50–90% less sludge production compared to the activated sludge process.[1] Although significant advances have been achieved in BES research in the last few years, BES is still under laboratory scale due to several technical barriers that include high capital cost of materials, microbial competition between electrode biofilm and planktonic cells for substrate, poor hydrolysis of particulate matters, electrode potential loss, membrane pH gradient etc.[3,4,8] A membrane will be an integral part for various value-added products (e.g. acetate, hydrogen peroxide) recovery from the cathode in BES. Rozendal et al. [4] reported that the cost of a membrane is almost 38% of the total capital cost of BES. Several literatures commonly reported BES challenges caused by a membrane, which are pH gradient, acidic pH in an anode chamber, O_2 diffusion, and H_2 loss.[9–12] Therefore, a focus on the development of more efficient and inexpensive membranes is indispensable for BES commercialization.

BESs use microorganisms usually to catalyse the electron transfer from electron donor to conductive solids (e.g. electrodes). These microorganisms are called exoelectrogens,[13] electrocigens,[14] anode-respiring bacteria (ARB),[15], or electrochemically active microorganisms.[16] This electron transfer occurs outside cells, so it is called extracellular electron transfer (EET).[3,8,17–20] Microbial EET allows us to only extract electrons from complex wastes and wastewaters, and the electrons are reduced on the cathode in BES. Therefore, we can manipulate cathodic compounds to our target value-added products. For instance, a microbial fuel cell (MFC) is able to generate electric power from the wastes and wastewaters, and O_2 is the cathodic electron acceptor for power generation. A traditional dual-chamber MFC consists of an anaerobic anode and aerobic cathode chamber partitioned by a membrane (Figure 1). In the anode chamber, microorganisms oxidize organic substrates anaerobically, and produce electrons, protons, and carbon-dioxide. A membrane acts as an electrolyte in chemical fuel cells where redox reactions mainly occur in the gas phase. In MFCs in which fuels are provided as liquid phase the membrane is a

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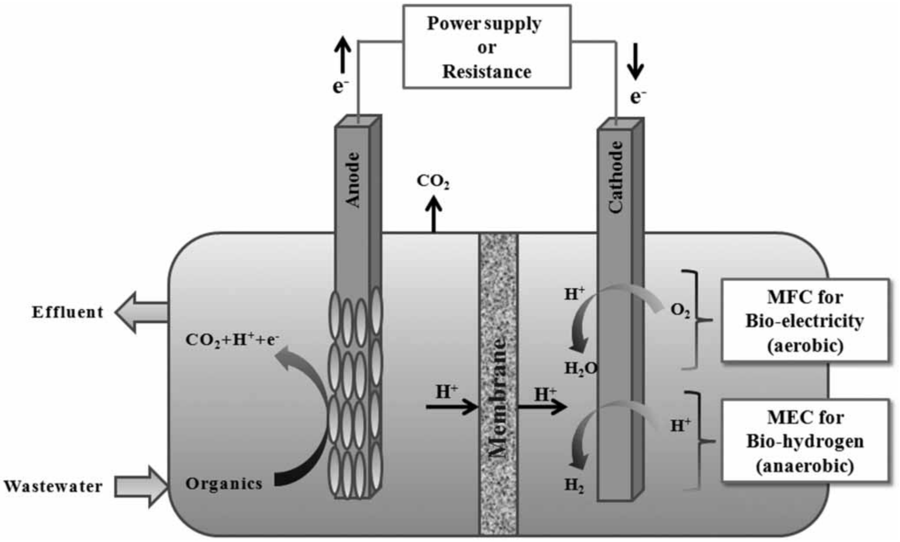

Figure 1. Bioelectrochemical cell (BES) for energy recovery.

part of the electrolyte and mainly works as a physical barrier between electrodes (e.g. O_2 transfer from the cathode to the anode). Hence, the membrane in the BES should have a high capacity of blocking the transfer of reactants or products between the two chambers, such as substrate, microorganisms, oxygen, hydrogen gas, and H_2O_2. For each electron that is released from the anode, an equivalent proton or other counter ions must be transferred between electrodes through the membrane to meet charge neutrality. Thus, the resistivity of the membrane to ion movement strongly affects power output in MFCs, hydrogen gas production rate, or the production rate of other value-added products (e.g. H_2O_2) against energy input as applied voltage in BESs. For example, the prevention of oxygen transfer from the cathode to the anode is a vital role of the membrane in MFCs because kinetically efficient ARBs (e.g. *Geobacter* sp.) are mainly anaerobes. Oxygen molecules diffused to the anode chamber stimulate the growth of aerobic bacteria, and these bacteria will reduce substrate electrons available to electricity generation.[11,21,22]

Recently, the concept of MFCs has been successfully modified for directly producing biohydrogen from substrate electrons produced by ARB, called a microbial electrolysis cell (MEC) (Figure 1). In the cathode of an MEC, the migrated electrons from the anode are used to reduce protons or water to hydrogen gas ($2\,H_2O + 4e^- \rightarrow 2OH^- + H_2$) on the cathode under anaerobic conditions [4,13] in which we must provide exogenous energy to boost up cathode potential for hydrogen gas production.[13,23] The presence of a membrane in MECs is also important to maintain high purity of hydrogen gas in the cathode. In MECs lacking a membrane we will recover low quality of hydrogen gas mixed with CO_2, CH_4, and H_2S produced in the anode chamber.[12] The recovery of hydrogen gas can substantially decrease in membrane-free MECs when hydrogenotrophic methanogens or acetogens actively transform hydrogen gas into methane gas or acetate.[3,24–26]

Most of the membranes used for BES, have been formerly developed and implemented for chemical fuel cells. Although a significant research effort has been underway to explore suitable membranes for BES, most of the reported a BESs used a proton exchange membrane (PEM) or a cation exchange membrane (CEM). To date, Nafion is the most commonly used PEM due to its highly selective permeability and conductivity to protons.[27–33] Nafion membrane allow not only proto but also other cations in the heterogeneous, complex wastewaters in which various ions are present.[29,34,35] The higher oxygen permeability of Nafion can inhibit ARB metabolism and deteriorate BES performance in terms of electrical power or hydrogen gas production. High costs of Nafion membrane are inappropriate for large-scale BES. To replace Nafion membrane researchers have introduced new membranes or separators more adequate for large-scale BES: CEM (Ultrex, Selemion, SPEEK etc.),[34,36,37] anion exchange membrane (AEM),[13,34,38,39] bipolar membrane,[40–42] charge mosaic membrane,[41] ultrafiltration membrane (UFM),[34,36,43] microfiltration membrane (MFM),[35,43,44], nano-porous membrane.[45,46] Although various types of membrane have been explored for BES application, researchers are still facing a number of challenges associated with membrane, such as increased internal resistance, oxygen leakage (in MFCs), substrate loss, pH gradient, membrane polarization, and biofouling (Figure 2).

The aim of this article presents a review on membranes used for BES, features advantages and disadvantages, and finally outlines the future research direction in the search for a suitable membrane for BES commercialization.

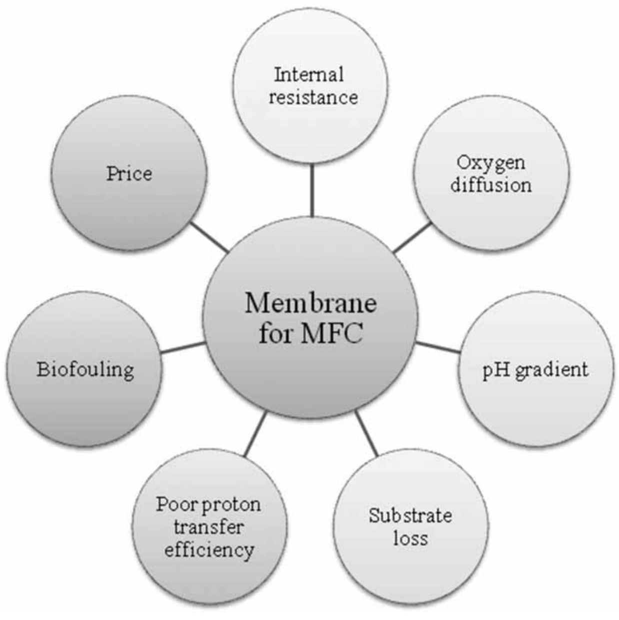

Figure 2. Major barriers of membranes for BES application.

2. Technical barriers of membranes for BES application

Several studies have addressed the role of membranes on a BES's overall performance. This section will introduce fundamental problems associated with membranes that affect the BES performance.

2.1. *Proton permeability and pH gradient*

Proton transfer rates from the anode to the cathode determine BES performance, when proton is the counter ion for charge neutrality. Therefore, proton transfer is one of the major constraints in BES operation using a proton or CEM. In BES, anodic reactions produce protons equivalent to electrons, and thus the transfer of cations other than protons acidifies the anode chamber, which can seriously inhibit ARB's metabolism.[8,47] Therefore, an ideal membrane for BES should have highly selective permeability of protons. Electrons transfer to the cathode depends on the potential gradient, while protons migrate to the cathode by electrical field and diffusion (concentration gradient). Concentration gradient for protons between two chambers is typically as small as 10^{-7}–10^{-8} M in BES so that proton transfer rates are lower than the electron transfer. Thus, proton transport rates through a membrane can be substantially low when proton permeability of the membrane is poor.[10] The proton mass transfer rate (n_H, mol/s) can be calculated using the following equation [48]:

$$n_H = k_H A \Delta c = \frac{D_H}{L} A \Delta c, \quad (1)$$

where, k_H is the proton mass transfer coefficient (cm/s), Δc is the concentration difference between two chamber (mol/cm^3), A is the mass transfer area (cm^2), L is the thickness of membrane (cm), D_H is the diffusion coefficient of protons (cm^2/s). Equation (1) suggests that using a membrane with lower thickness can be an effective approach to enhance proton transport from the anode to the cathode Table 1 shows the mass transfer coefficients of various cations calculated for different membranes. Thus, theoretically membranes with lower thickness (e.g. Selemion, Nafion, MFM, etc.) should provide higher mass transfer rate for protons compared to other cations, as diffusion coefficient of protons is much higher compared to other cations. However, due to the very small proton concentration gradient between the anode and the cathode in BES, we usually see very low proton mass transfer rates in BES. Besides protons, other cations or anions (cations: Na^+, K^+, Ca^{2+}, Mg^{2+}, and NH_4^+; anions: Cl^-, SO_4^{2-}, CO_3^{2-}, and PO_4^{3-}), of which concentration gradients are three to four orders of magnitude higher than protons, would transfer through the membrane for charge neutrality between the two chambers. Several studies [31,49] reported that dual-chamber MFCs with PEM did not only allow protons to transfer, but other abundant cations to move to the cathode for charge neutrality. Increasing pH difference between the anode and the cathode could be a possible approach to enhance proton permeability through the membrane; however, this approach is limited by pH gradient causing potential loss in BES (discussed later). For a specific membrane, increasing mass transfer area or membrane surface area would also allow higher proton permeability. However, membrane surface area is limited by the BES architecture (electrodes surface area, membrane electrode assembly etc.).

pH gradient can adversely affect BES performance. First, the pH gradient causes potential loss. According to the Nernst equation, the potential loss due to pH gradient is 59 mV per pH unit. Due to the pH gradient-related potential loss, voltage of ~0.2 V is lost in MFCs or additional energy (~0.13 kWh/m^3 H_2 per pH unit) must be supplied for MECs.[13] Second, the pH gradient can acidify an anode chamber in BES using the CEM because Na^+, K^+, Ca^{2+}, Mg^{2+}, or NH_4^+ move to the cathode, instead of protons. As a result, protons accumulate in the anode chamber and ARB metabolism will be seriously inhibited. Franks et al. [47] reported that current significantly drops from 7.5 mA (at pH~7 in the anode chamber) to 3.5 mA at pH of around 6. To acclimate acidic ARB on the anode can be a solution to the proton accumulation in the anode. A few literatures reported acidic ARB at pH 4–6,[51,52] but it is questionable to use acidic ARB in large BESs that need high current density over 10 A/m^2.[9,53] Finally, transferred cations can form chemical precipitates (e.g. calcium phosphate) on the surface of the membrane or on the cathode, and these precipitates would increase ohmic loss or deteriorate cathodic reactions.[54]

Proton accumulation in the anode chamber can permanently damage BES performance because acidic pH seriously inhibits or inactivates ARB metabolism. To our

Table 1. Mass transfer coefficients (K) for various ions through different membranes.

Membrane	Thickness (mm)	$K(\times 10^{-5}$ cm/s)[a] H^+	Na^+	NH_4^+	Ca^{2+}	Mg^{2+}	K^+
Nafion	0.19	490	70	103	42	37	103
CMI-700	0.46	202	29	43	17	15	43
SPEEK	0.20	466	67	98	40	36	98
Selemion	0.15	621	89	131	53	47	131
AEM-7000	0.18	517	74	109	44	39	109
UFM	0.33	282	40	59	24	22	59
MFM	0.17	564	81	119	48	43	119

[a] K (cm/s) values were calculated based on typical diffusion coefficients of different ions in water at 25°C: H^+ (9.31×10^{-5} cm^2/s), Na^+ (1.33×10^{-5} cm^2/s), NH_4^+ (1.96×10^{-5} cm^2/s), Ca^{2+} (0.79×10^{-5} cm^2/s), Mg^{2+} (0.71×10^{-5} cm^2/s), K^+ (1.96×10^{-5} cm^2/s). Data collected from [50].

experience and knowledge ARB are not typically recovered after ARB are inhibited by unfavourable growth conditions for several weeks, such as low pH, lack of substrate, low temperature, and so on. Therefore, maintaining neutral pH in the anode chamber is essential when substantial pH gradient across the membrane occurs in BES. BES using PEM or CEM cannot avoid proton accumulation in the anode chamber, and thus many studies have used high buffer medium in a range of 50–100 mM phosphate buffer.[9,38] Some wastewater streams where proteins are rich (e.g. poultry wastewater, animal manure, etc.) may not have a low pH issue in the anode due to NH_3 (aq) release from protein hydrolysis. Hence, PEM- or CEM-BES would be ideal for protein-rich wastewaters if particulate matters in these wastewaters would not foul the membrane or the anode. Recycling catholytes (high pH) into the anode chamber (low pH) can neutralize protons produced in the anode (Figure 3(a)), but dissolved oxygen (DO) will seriously inhibit ARB metabolism in MFCs – substantial loss of substrate electrons to H_2O when oxygen acts as electron acceptor in the anode chamber. In comparison, catholyte recycling to the anode can work for MECs that produce hydrogen gas in the cathode, due to the lack of DO. However, H_2 loss would be significant if dissolved hydrogen is oversaturated in catholytes.[24] Catholyte recycling does not work for dual-chamber BESs that produce other value-added products on the cathode (e.g. H_2O_2, acetate, ethanol, etc.). Anolyte recycling to the cathode would not be feasible for pH gradient minimization, as we are interested to recover value-added products from the cathode (i.e. acetate, H_2O_2) (Figure 3(b)). Torres et al. [55] proposed the circulation of CO_2 from the anode to the cathode for mitigating the pH gradient between the two chambers of a BES using an AEM (Figure 3(c)), where HCO_3^- or CO_3^{2-} in the cathode transfers to the anode for charge neutrality, instead of OH^-; the pH gradient between the two chambers was as small as two units (120 mV energy loss) even at 1.9–2.8 W/m^2 of high-power density. CO_2 circulation can attenuate the pH gradient at high current density for the BES producing value-added products (Figure 3(c)). One bottleneck of this approach would be a small volume of carbon dioxide produced from the anode due to neutral pH in the anode. For instance, the majority of inorganic carbon form is HCO_3^- (~90%) at pH 7.3 in the anode when ARB oxidize glucose to carbon dioxide; CO_2 is only 10% of the inorganic carbon. The glucose oxidation releases 24 mol protons per mol of glucose, and thus the molar ratio of CO_2 to protons in glucose oxidation is 1:40 at pH 7.3. Thus, the supply of exogenous CO_2 (g) to the cathode is essential. To meet the charge balance in dual-chamber MFCs, ammonium ions (NH_4^+) can be transported to the cathode across the CEM.[49] Ammonium ions (NH_4^+) can be recycled as ammonia gas from the cathode to the anode to avoid the proton accumulation in the anode (Figure 3(d)).[56,57] However, deprotonation and stripping of ammonia (pK_a 9.3) would need high pH in the cathode.

2.2. *Oxygen diffusion from the cathode to the anode*

Oxygen permeability of membrane is a major concern for MFCs as kinetically efficient ARB (e.g. *Geobacter* sp.) are normally strict anaerobes. Electrons that can be recovered as value-added products (electricity or hydrogen peroxide using O_2 as the electron acceptor to the cathode) will be lost as H_2O when aerobic or facultative bacteria take up the electrons and utilize diffused electron oxygen from cathode as the terminal electron acceptor in the anode. Thus, oxygen diffusion to the anode seriously decreases columbic efficiency (coulombs over consumed substrate-electrons) and aerobic or facultative bacteria would outcompete ARB for anode biofilm due to relatively high biomass yield. This microbial competition can be critical for long-term operation of MFCs. Planktonic aerobic or facultative bacteria (e.g. *Shewanella, Pseudomonas, Ochrobactrum, and Escherichia* spp.) that are able to scavenge oxygen molecules mitigate oxygen inhibition on the ARB biofilm anode.[58–60] However, MFCs are typically designed to decrease electrode distance for minimizing ohmic resistance (mainly ion transfer resistances for charge neutrality), which means that aerobic or facultative bacteria have more opportunities to grow on the anode biofilm as a consequence of O_2 diffusion from the cathode. Based upon the conductive biofilm matrix to EET, non-ARB growth on the biofilm anode would increase resistances to EET.[3,8,61] Even for the shuttling mechanism, the proliferation of non-ARB would dilute the concentration of shuttling compounds in the biofilm anode; the concentration gradient for shuttle diffusion becomes smaller, and current would decrease significantly.

Oxygen diffusion can be minimized by maintaining the aeration in the cathode chamber to a minimum level,[27] but this approach will limit O_2 concentration for the cathode, decreasing cathode potential (−0.42 V to −0.17 V vs. Ag/AgCl). This concentration limitation is also critical for hydrogen peroxide (H_2O_2) synthesis where maintaining high oxygen concentration (3×10^{-7} mol/cm^3) in the cathode chamber is required.[62] Sulphonated polyether ether ketone (SPEEK) membrane showed the lowest oxygen permeability (0.024×10^{-4} cm/s) among various membranes used for BES application (Table 2), while power density (670 vs. 300 mW/m^2) and columbic efficiency (75% vs. 50%) were substantially higher compared to Nafion 117.[37] Thus, a membrane or separator that has low permeability (e.g. 0.024×10^{-4} cm/s) to oxygen molecules is essential for a BES using O_2 as the electron acceptor in the cathode.

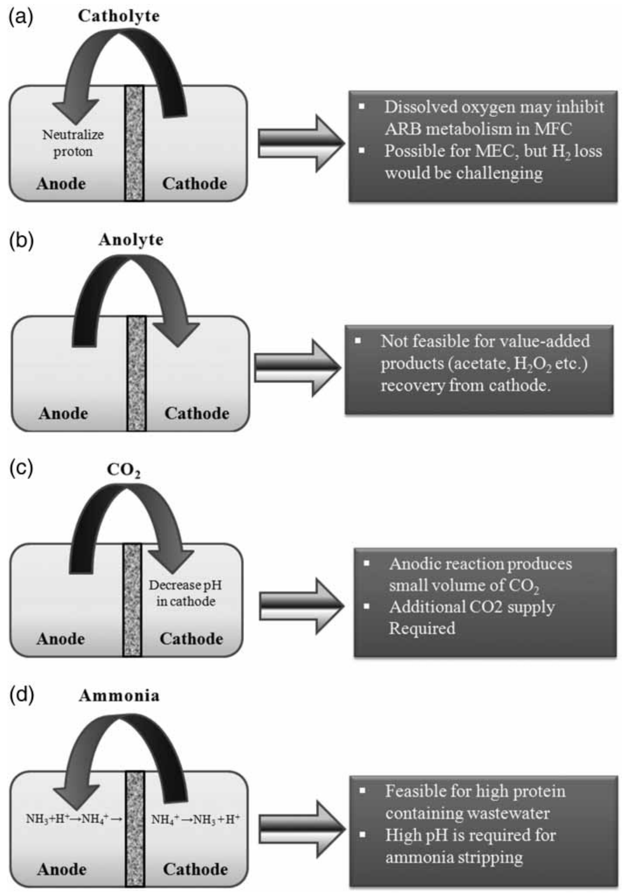

Figure 3. Possible approaches for pH gradient minimization in bioelectrochemical cells and their limitations.

Table 2. Mass transfer and diffusion coefficients of oxygen for various membranes.

Membrane	Thickness (mm)	Porediameter (μm)	Oxygen mass transfer coefficient, $K_o(\times 10^{-4}$ cm/s)	Oxygen diffusion coefficient, $D_o(\times 10^{-6}$ cm^2/s)	References
Nafion 117	0.19	–	1.4	2.7	[35]
Nafion 117	0.19	–	2.05	3.89	[43]
Nafion 117	0.19		1.3	2.4	[34]
Nafion 117	0.19	–	0.16	0.3	[37]
Nafion 117	–	–	2.8	5.35	[11]
Nafion	0.18	–	0.50	0.90	[36]
SPEEK	0.20	–	0.024	0.048	[37]
CEM (CMI-7000)	0.46	–	0.94	4.3	[34]
Selemion	0.15	–	0.05	0.08	[36]
AEM (AMI-7001)	0.46	–	0.94	4.3	[34]
AEM (AFN)	0.15	–	1.26	1.9	[63]
AEM (AM-1)	0.14	–	0.98	1.4	[63]
AEM (ACS)	0.18	–	0.65	1.2	[63]
UFM-0.5K	0.265	–	0.19	0.51	[34]
UFM-1K	0.265	–	0.41	1.1	[34]
UFM-1K	0.40	–	2.11	8.44	[43]
UFM-3K	0.265	–	0.42	1.1	[34]
UFM-5K	0.40	–	2.14	8.57	[43]
UFM-10K	0.40	–	2.24	8.95	[43]
MFM	0.13	0.45	5.9	7.7	[35]
MFM	0.20	–	4.98	9.96	[43]

2.3. Substrate loss in the anode chamber

In addition to substrate loss by oxygen diffusion present in the anode chamber, there could be another route of substrate loss because of the diffusion of substrate through the membrane in dual-chamber BESs. In dual-chamber BESs, the substrate can diffuse from the anode to the cathode because of a substantial concentration gradient of $\sim 10^{-2}$–10^{-3} M.[34] As substrate for ARB, many studies have used simple acids (e.g. acetate, propionate, or their mixture) that are deprotonated and have negative charge at neutral pH; pk_a values for those acids range from 4.75 to 4.87. Negatively charged acids may not transfer to the cathode through the CEM. Therefore, the substrate loss in PEM- or CEM-BES would be negligible. In contrast, substrate loss by the diffusion would be significant in AEM-BES, since AEM facilitates transfer of anions from the anode to the cathode.[40] Kim et al. [34] found that loss of coulombs due to the acetate diffusion through the membrane into the cathode chamber is 3.7 times higher in the AEM-BES than in the CEM-BES. Based on coulombic balance, highest substrate loss (up to 7%) through acetate diffusion was observed for UFM with molecular cutoff weights of 3 K Daltons among the AEM, CEM, and Ultrafiltration membrane (UFM) (0.5, 1, and 3 K). This substrate loss cannot be avoided in AEM-BES even when we use complex wastewaters as feed due to fermentation. Conjugate bases of acids (e.g. acetate, propopinate, butyrate, etc.) accumulated by fermentation of the wastewaters can diffuse to the cathode before ARB use them, which may bias coulombic efficiency (CE) in AEM-BES. There are no published articles that clearly show the transfer of these conjugate bases, but AEM can allow their transport to the cathode.[12] Substrate loss through diffusion may not be substantial compared to the substrate loss via anaerobic fermentative and planktonic aerobic or facultative bacteria in short-term experiments.[34] In long-term tests, however, substrate loss can be significant when membrane structure would be partially damaged, due to low pH or chemical precipitation.[42]

2.4. Membrane resistance

Ion-transport resistance or transfer limitation of cations through the membrane plays an important role in the internal resistance of BESs.[64,65] Electrochemical impedance spectroscopy (EIS) has been used as a tool to identify the exact contribution of the membrane's resistance in the BES's total internal resistance.[66] Literatures showed that the ion-transport resistance through membranes consists of the membrane's resistance and the resistances from the electric-double layer at the membrane surface and the diffusion boundary layer.[63,67,68] Ji et al. [63] found that the resistances from the electric-double layer and diffusion boundary layer were the main resistances, as compared to that from the membrane. Oh and Logan [69] have also found that membrane resistance makes a small contribution to the total internal resistance of an MFC, and a slight increase in the membrane internal resistance would not significantly impact the performance of the MFC. We could mitigate the resistance caused by the diffusion boundary layer under intensive mixing conditions for bench-scale BES, but its economical efficiency would be doubtful in large-scale BESs, due to substantial energy input for increasing mixing conditions. To manipulate the membrane surface area would be more practical and economical, since the surface area can affect internal resistance in BESs.

Membrane resistance (R_m, Ω) is inversely proportional to the membrane surface area, and can be expressed as following [65]:

$$R_m = \frac{r_m}{s_m}, \tag{2}$$

where, r_m is the area-specific resistance of membrane ($\Omega\,\mathrm{cm}^2$) and S_m is the surface area of the membrane (cm^2). Oh and Logan [69] found that the power output in an MFC is a function of the PEM surface area, as the MFC internal resistance decreases with the increase of PEM surface area. They reported that for a fixed anode and cathode surface area (22.5 cm^2) the increase in PEM surface area from 3.5 to 30.6 cm^2 increased the power density from 45 to 190 mW/m^2. In a further study, Zuo et al. [70] also observed an increase in power density from 306 to 403 mW/m^2 for increasing membrane surface area from 13 to 27 cm^2 at a constant anode surface area (7 cm^2), while internal resistance increased from 80 to 130 Ω. Thus, the ratio of membrane surface area to the electrode surface area would be important for the power output, and membrane surface area may limit the power output when the membrane surface area is smaller than that of the electrodes, due to an increase in internal resistance.[69,70]

2.5. Membrane biofouling and deformation

Membrane biofouling can have an adverse impact on the performance of BESs, due to increasing resistance for ion transfer. Membrane biofouling is an inevitable process in BES operation because of biofilm formation during long-run operation.[11] Biofouling depends on the surface topology of the membrane, and usually a rough surface is more vulnerable to biofilm formation compared to the smooth surface.[45] Biofilm is mainly composed of microorganisms, extracellular polymeric substances, soluble microbial products, and inorganic salts.[54,64,71] To date, few studies investigated the impact of biofouling of membranes on the performance of MFCs.[11,64,68,71] Xu et al. [64] reported that biofouling significantly reduces the ion exchange capacity, conductivity, and diffusion coefficients of cations, which can reduce power generation in an MFC operated with a fouled membrane.[64] Proton transfer limitation due to membrane fouling increases pH in the cathodic chamber, and potential losses by pH gradient significantly deteriorates MFC performance.[12,72] Compared to a BES operated with virgin Nafion 117, Xu et al. [64] reported 32% decrease in maximum power output for Nafion 117 membrane fouled by microorganisms, EPS, or inorganic salts.

To achieve sustainable power output from BESs, a fouled membrane needs to be replaced [64] or regularly cleaned.[71] Choi et al. [71] have reported that physical brushing is not enough to recover BES performance, and have recommended cyclic chemical cleaning to remove biofilm on a fouled membrane or to regenerate the functional group of the membrane. Various chemicals (e.g. citric acid, NaOCl, HOCl, H_2O_2, etc.) can be used to remove biofilm and chemical precipitates from the membrane surface as well as to regenerate the functional group of the membranes.[73] Biofilm is normally formed in the anode side, which means that we should inject chemicals into the anode chamber for membrane cleaning. These chemicals would seriously inhibit ARB metabolism. High concentration of planktonic cells present in the anode chamber could first react with these chemicals in MFCs fed with complex forms of organics (e.g. domestic and industrial wastewaters), which act as chemical scavengers. However, it seems challenging to balance non-ARB and ARB growth in the anode for this purpose. Most of the dual-chamber BES configurations use a flat-sheet-type membrane instead of a hollow fibre membrane, and the membrane is usually sandwiched between the anode and the cathode. Therefore, maintenance cleaning (i.e. backwashing with or without chemicals) cannot be performed to get rid of the foulants, and recovery cleaning methods (e.g. physical cleaning with brush, soaking in cleaning chemicals) can be used for maintenance. However, the membrane has to be taken out from the BES for recovery chemical cleaning. The technical challenge would be how to clean the fouled membrane regularly without deteriorating the biofilm anode. ARB are exposed to air when we take the membrane out of the BES for cleaning.

After long-term operation of the BES, membrane deformation may occur due to membrane swelling during ion transport through the membrane.[74] Enhanced internal resistance as a result of accumulation of protons (i.e. anolyte having low pH) and gas (e.g. CO_2) in the void space created between the deformed membrane and electrode may substantially reduce the power output of the BES.[74] Membrane electrode assembly (MEA) has been found to be very effective for minimizing membrane swelling along with higher power output due to reduced electrode spacing and ohmic loss.[74–76] Zhang et al. [74] have found an MEA where a stainless steel membrane used to press the membrane flat against the cathode to avoid membrane deformation with enhanced power output from 16 to 46 W/m^3in AEM-BES.

3. Membranes for BES

Ion exchange membranes (IEMs) contain fixed anionic or cationic exchange functional groups that allows ion transfer or separation. Ion transfer for charge neutrality is essential for BESs when current is generated. For this reason, many researchers have used IEM as a separator between two chambers in BES. In this section we will feature membranes used for BESs, focusing on IEM (PEM, AEM, bipolar membrane, and charge mosaic membrane), and introduce other types of membrane (UFM, MFM, and nanocomposite membrane).

3.1. Proton exchange membrane

Proton exchange membranes are characteristically based on polymer electrolytes with negatively charged acidic functional groups attached to their polymer backbone.[77] The negatively charged groups allow the transfer of cations from the anode chamber to the cathode chamber (Figure 4(a)). Therefore, PEMs are also referred to as CEMs; they are practically cation specific membrane. Most of the BES have used the CEM or PEM, probably because initial BESs work mimicking hydrogen fuel cells using the PEM. Among various CEMs, Nafion is the most widely used due to its excellent ionic conductivity (10^{-2} S cm^{-1}).[78] Nafion is a sulphonated tetrafluorethylene copolymer, and consists of a hydrophobic fluorocarbon backbone ($-CF2-CF2-$) to which hydrophilic sulphonate groups (SO_3^-) are attached.[79] The presence of negatively charged sulphonate groups (SO_3^-) in the Nafion is responsible for the high level of proton conductivity.[80,81] Usually BES is operated at a neutral pH where ARB metabolism is optimized. The cation species (Na^+, K^+, Ca^{2+}, Mg^{2+}, and NH_4^+) contained in the anolyte are typically present at 10^4–10^5 times higher concentration than protons, and these cations combine with the sulphonate groups of the Nafion membrane. As a result, proton transport is seriously limited and a pH gradient occurs in dual-chamber BESs.[31] Nafion is permeable to substrate (acetate) and oxygen, which may deteriorate MFC performance.[11] Rozendal et al. [82] reported that the diffusion of hydrogen gas from the cathode to the anode chamber through the Nafion 117 membrane can significantly reduce hydrogen recovery in MECs. Besides, Nafion 117 has a very poor ability to prevent pH gradient during MEC operation, as compared to other IEMs (AEM, CEM, and Bipolar membrane (BPM)).[12,41] For a long-term operation Nafion has lower resistance to fouling,[11,64] but the high cost (1400–1500 US $\$/m^2$) of Nafion would be a major barrier to large-scale BESs; the fluorochemistry involved in Nafion synthesis (e.g. perfluorinated polymers based on perfluorosulphonic acid) substantially increase the expense.[4,77]

Ultrex CMI-7000 containing the sulphonic acid ($-SO_3H$) group is a cost-effective CEM (Table 4), and showed potential to be a suitable alternative to Nafion PEM.[34,84] In addition, CMI-7000 showed lower oxygen mass transfer coefficients than Nafion (Table 2). Kim et al. [34] reported that the Ultrex CMI-7000 membrane is capable of producing comparable performance to Nafion.

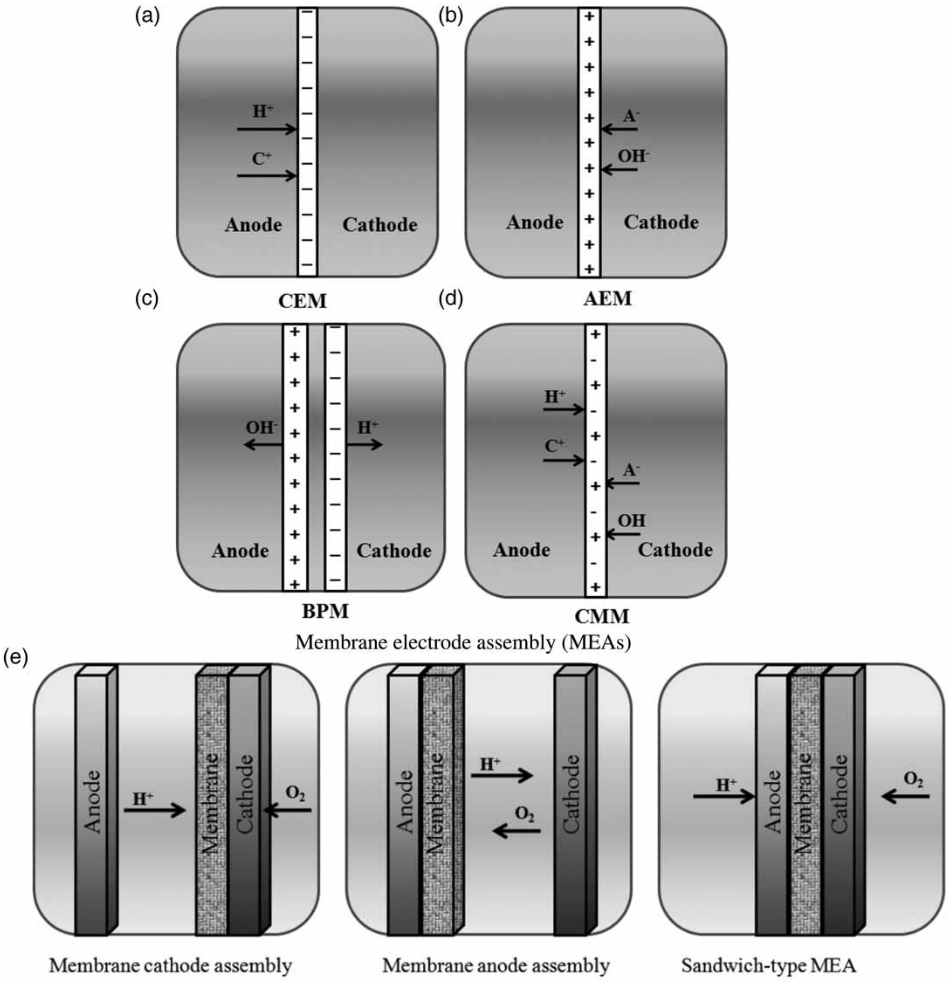

Figure 4. (a) proton exchange membrane, (b) AEM, (c) bipolar membrane, (d) charge mosaic membrane, and (e) various membrane electrode assembly (figure drawn with modifications after Rozendal et al. [41] and Fan et al. [83]).

The power density and CE of an MFC using Nafion were 514 mW/m^2 and 41–46%, respectively, while for an MFC using CMI-7000, they were 480 mW/m^2 and 41–54%, respectively. Selemion is a hydrocarbon type PEM developed and manufactured by Asahi Glass Co., Japan. Selemion has been found as a suitable alternative to Nafion 117 which can provide lower internal resistance, lower oxygen permeability and lower cost.[36] Lefebvre et al. [36] reported 25% more power densities with an MFC operated with Selemion as compared to Nafion. Ayyaru and Dharmalingam [37] used SPEEK as the PEM for MFC application. SPEEK has been developed through the sulphonation of the polyether ether ketone (PEEK) membrane to achieve higher proton conductivity. Their study showed that oxygen permeability of SPEEK is one order of magnitude lower than that of Nafion 117 (Table 2), along with enhanced power generation and lower substrate loss during MFC operation. The aforementioned studies suggested that Ultrex, Selemion, and SPEEK can be good replacements of Nafion 117 in terms of low cost and less oxygen diffusion coefficients (Tables 2 and 4).

3.2. Anion exchange membrane

AEMs consist of polymer networks containing immobilized, positively charged groups that allow them to selectively transport anions from the cathode to the anode chamber [40] (Figure 4(b)). For BESs operated with AEM, typically electroneutrality is met by OH$^-$ transfer from the cathode to the anode. However, AEM was recently found to substantially increase BES's performance due to the enhanced proton transfer across the membrane by negatively charged chemical buffers, such as phosphate and bicarbonate alkalinity.[13,34,38,39] The protons produced by microbial oxidation of organics at the anode chamber may react with the phosphate buffer to form monobasic phosphate.[38] Monobasic phosphate may easily transfer from the anode to the cathode through AEM. Finally, monobasic phosphate can transfer back to the cathode as phosphate buffer.[38] The mechanism of proton transfer by phosphate and bicarbonate is shown in Figure 5. Several studies reported that the AEM can perform better than intensively used PEM/CEM in terms of maintaining lower pH gradient across the membrane,[34,41] lower ion transport

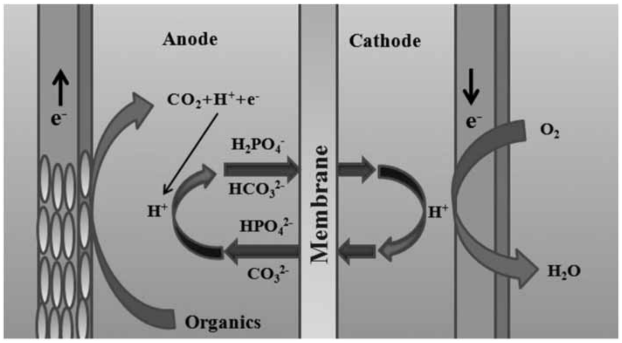

Figure 5. Proton transfer by phosphate and bicarbonate (figure drawn with modifications after Fan et al. [38]).

resistance,[23] and reduced tendency to biofouling due to the precipitation of transported cations on the cathode surface.[54]

Kim et al. [34] investigated the performance of an AEM (AMI-7001, Membrane International Inc., NJ) in a dual chamber MFC filled with nutrient media with phosphate buffer (50 mM, pH 7.0), and compared its performance with Nafion 117, CEM (CMI-7000), and UFMs with three different molecular weight cut offs of 0.5, 1, and 3 K Daltons (see the literature [34] for more information). Among different types of membranes, AEM showed the best performance: the largest power density (610 mW/m^2) and the highest CE (72%), due to enhanced proton transfer facilitated by phosphate anions and lower internal resistance. Their results also suggested that AEM maintained a charge balance through the redistribution of phosphate ions across the membrane; while orthophosphate anion species (HPO_4^{2-} and $H_2PO_4^-$) buffered the pH drop in the anode chamber. Rozendal et al. [12] applied AEM in an MEC, and found that AEM is better than CEM in terms of attenuating pH gradient between the two chambers (CEM $\Delta pH = 6.4$; AEM $\Delta pH = 4.4$). For CEMs, usually cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, and NH_4^+) move through membrane and may precipitate on the surface of the cathode that reduce the current. However, the AEM primarily allows anions to move from the cathode to the anode to maintain charge neutrality. Therefore, the possibility of cation precipitation on the cathode surface is much lower for AEM-BES. Mo et al. [54] reported that using AEM in an MFC may help to maintain stable power generation and membrane resistance attributed to small cation precipitation on the cathode surface because AEM efficiently impaired cation transport from the anodes.

Rozendal et al. [12] found that AEM (Fumasep®-FAB, FuMA-Tech GmbH, Germany) has better capability of preventing the pH gradient between two chambers than CEM (Nafion 117), and hence potential loss by pH gradient becomes smaller in AEM. Rozendal et al. [41] used AEM (Fumasep®FAB, FuMA-Tech GmbH, Germany) in an MEC operated with wastewater, and the MEC showed the best hydrogen production efficiency among four different types of IEMs. Sleutels et al. [23] reconfirmed that AEM (Fumasep®FAA, FuMA-Tech GmbH, Germany) can perform better than CEM (Fumasep®FKE, FuMA-Tech GmbH, Germany) in MECs. Their results showed that with constant applied voltage (1 V), biohydrogen production efficiency was significantly higher for the MEC operated with AEM (0.5 kwh/m^3 H_2) than CEM (2.5 kwh/m^3 H_2) due to lower ion transport resistance. Thus, in most of the BES studies, AEM performed better than CEM due to neutral pH maintenance in the anode chamber, less pH gradient between two chambers, and less cation precipitates on the membrane surface.

3.3. *Bipolar membrane*

The BPM consists of an anion selective layer and a cation selective layer joint together in series (Figure 4(c)).[87] The region between the anion and cation exchange layer is known as the transition region.[40] BPM offers a simultaneous migration of protons and hydroxide ions produced by water splitting at the transition region. BPMs have been used for MFC application.[40–42] Heijne et al. [42] reported that the use of BPM maintained the lowest pH in cathode in long term operation, due to water splitting reactions, which allows a small change of pH in the cathode between 2 and 2.5. In contrast, for an MFC operated with Nafion 117, catholyte pH increased very rapidly from 7 to 8.5 in their earlier study.[31] Rozendal et al. [41] also reported that the electrochemical performance (i.e. cumulative biohydrogen production) of BPM (FumaSep FBM, FuMA-Tech GmbH, Germany) was very poor among four types of IEMs (CEM, AEM, BPM, and charge mosaic membrane (CMM)) during MEC operation, although BPM showed the slowest increase in cathode pH. However, Harnisch et al. [40] reported that BPM does not prevent the pH gradient in MFCs due to large leakage, or ion flux occurs due to the migration of electrolyte ions to the transition region. Therefore, the mitigation of pH gradient in BES with BPM can be lower. In this review we did not find any significant benefit of BPM, as compared to other IEMs.

3.4. *Charge mosaic membrane*

The CMM consists of small negatively and positively charged ion exchange domains arranged in parallel.[87] As shown in Figure 4(d), CMM is permeable to both anions and cations. Rozendal et al. [41] used a commercial CMM (Dainichiseika Color & Chemicals, Co. Ltd., Japan) in an MEC using wastewater as substrate for biohydrogen production. Based on electrochemical performance (i.e. biohydrogen production) and proton transfer efficiency, CEM and AEM were better than CMM. Besides, CMM showed lowest ability to prevent pH gradient between two chambers among four types of IEMs (CEM, AEM, BPM, and CMM). Their study also showed that the CMM practically acts like a CEM, and facilitates more cation transfer

Table 3. Mass transfer and diffusion coefficients of substrate for various membranes.

Membrane	Thickness (mm)	Substrate mass transfer coefficient, K_s (cm/s)	Substrate diffusion coefficient, D_s (cm^2/s)	Substrate	References
Nafion 117	0.19	7.72×10^{-10}	1.47×10^{-11}	Congo red	[43]
Nafion 117	0.19	4.3×10^{-8}	0.82×10^{-9}	Acetate	[34]
CEM (CMI-7000)	0.46	1.4×10^{-8}	0.66×10^{-9}	Acetate	[34]
AEM (AMI-7001)	0.46	5.5×10^{-8}	2.6×10^{-9}	Acetate	[34]
UFM-0.5K	0.265	0.89×10^{-8}	0.24×10^{-9}	Acetate	[34]
UFM-1K	0.265	16×10^{-8}	4.2×10^{-9}	Acetate	[34]
UFM-1K	0.40	6.18×10^{-9}	2.47×10^{-10}	Congo red	[43]
UFM-3K	0.265	2.7×10^{-8}	7.2×10^{-9}	Acetate	[34]
UFM-5K	0.40	1.13×10^{-7}	4.51×10^{-9}	Congo red	[43]
UFM-10K	0.40	3.27×10^{-7}	1.31×10^{-8}	Congo red	[43]
MFM	0.20	5.08×10^{-5}	1.02×10^{-6}	Congo red	[43]

rather than anion transfer. Based on extensive literature search, no other studies could be found on the application of the charge mosaic membrane for BESs.

3.5. *Ultrafiltration membrane*

The UFM has been widely used in water and wastewater treatment to separate particulate contaminants using their different molecular cutoff weights (in Daltons).[43] Since UFM is permeable to anions and cations, UFM has also been used to separate fluid between the anode and the cathode in BESs.[34,36,43] Kim et al. [34] investigated the performance of UFMs with three different molecular cutoff weights of 0.5, 1, and 3 K Daltons in two different types of dual chamber MFCs (aqueous cathode and air cathode) using acetate as substrate. Compared to Nafion 117, CEM (CMI-7000) and AEM (AMI-7001), three UFMs showed lower oxygen mass transfer coefficients (Table 2). However, two of these UFMs (UFM-1 K and UFM-3 K) had relatively higher substrate mass transfer coefficients (Table 3). Overall, MFCs operated with UFMs produced relatively low power densities and low coulombic efficiencies (8.9–44.7%). Hou et al. [43] used three different UFMs with molecular cutoff weights of 1, 5, and 10 K Daltons to investigate the effect of the membrane on the performance of an MFC for simultaneous azo dye decolorization and electricity production. Compared to the MFM, three UFMs showed significantly lower oxygen and substrate mass transfer coefficients (Tables 2 and 3). However, among three types of membranes, Nafion 117 showed the lowest oxygen and substrate mass transfer coefficients. Although Nafion 117 resulted in highest CE, power density was significantly lower due to the high internal resistance. On the other hand, MFC operated with UFM-1 K produced 74% higher power density compared to the MFC operated with Nafion 117. Although UFM showed promising performances compared to PEM, more research would be required to optimize the thickness and pore size of UFM to improve coulombic efficiencies and substrate loss.

3.6. *Microfiltration membrane*

The MFM (~0.1 μm in pore size) has been successfully used to separate microorganisms, emulsions, colloids, dispersed material, and suspended solids from water. The MFM has been also used to separate microorganisms from the cathode in BESs.[35,43,44] The effect of MFMs on MFC performance was investigated by Sun et al. [44] and Hou et al. [43] Tang et al. [35] applied cellulose acetate MFM in dual-chamber MFCs using acetate as substrate, and compared its performance with Nafion 117. Although MFM was able to minimize the pH gradient and maintain similar ranges of internal resistance and power density to Nafion 117, CE was much lower as a result of higher oxygen diffusion through the MFM from the cathode to the anode. Some literatures presented high power density with low to moderate CE,[35,43,44] which indicates that MFM would be applicable for MFCs. A long-term performance is, however, questionable in MFM-MFCs because consistent exposure of O_2 to the ARB can finally shift ARB biofilm on the anode into aerobic biofilm in which power would be negligible. MFM would be used for MECs for hydrogen gas production on the cathode, but hydrogen molecules would be easily transferred to the anode, substantially reducing hydrogen yield.

3.7. *Nanocomposite membrane*

In the past few years, the nanocomposite membrane showed huge potential in energy, environment, and biomedical applications, due to their unique mechanical and thermal properties, and a large surface area. The distribution of nanoparticles in the polymer matrix changes the chemical and physical properties of traditional polymeric membranes. Nanoparticles can significantly improve separation efficiency by generating improved penetration paths for desired species and preventing the transport of undesired species.[88] Recently, nanocomposite membranes have been employed in BESs, and they showed promising performance compared to the traditional PEMs.[45,46]

Rahimnejad et al. [45] synthesized nanocomposite membranes using Fe_3O_4 nanoparticles and compared their efficiencies to Nafion 117 in dual-chamber MFCs. They fabricated Fe_3O_4/polyethersulphone (PES) nanocomposite membranes with four different weight percent of Fe_3O_4 (5%, 10%, 15%, and 20%) in PES matrix, and membrane with 15wt% of Fe_3O_4 nanoparticles produced 29% more power than Nafion 117. Ghasemi et al. [46] synthesized carbon nanofiber (CNF)/Nafion and activated carbon nanofiber (ACNF)/Nafion nanocomposite membranes and compared their feasibility to Nafion 112 and Nafion 117 in dual chamber MFCs. They reported that the CNF significantly reduced the roughness, pore size and porosity of the membranes, and as a result enhanced the membrane performance for BES application. The reduced pore size minimized the oxygen back diffusion from the cathode to the anode and substrate loss from the anode chamber.[46] In addition, reduced roughness of membrane mitigated biofouling problems. The maximum power produced for CNF/Nafion and ACNF/Nafion membranes were 47.48 and 57.64 mW/m^2, respectively; while for MFC using traditional Nafion 112 and Nafion 117 membranes, maximum power production was 13.99 and 38.30 mW/m^2, respectively.[46]

3.8. *Membrane electrode assembly*

The arrangement of the membrane in the BES architecture may significantly influence the power output.[89,90] Membrane electrode assembly (MEA) is a novel design where membrane is bounded (with or without bounding material) to the electrode or sandwiched between two electrodes.[75] In addition to reduced electrode spacing, MEAs may reduce ohomic resistance with enhanced proton transfer through the membrane. Zuo et al. [91] found that using MEA configuration in a tubular BES may reduce ohomic resistance by 22% with improved cathode potential and higher power density (17.7 W/m^3) compared to a cube reactor configuration (9.9 W/m^3). Liang et al. [92] also reported that reduced electrode spacing due to MEA configuration may substantially enhance MFC power output from 354 to 1180 mW/m^2. However, using binding materials used for MEAs may introduce additional internal resistance to BESs.[75] Several conductive binding materials such as graphite, nickel paint, and non-precious metal catalysts (e.g. MnO_2) may solve this problem.[91,93] Kim et al. [76] also found that using hydrogel as binding material in MEA configuration in a tubular MFC may significantly help to minimize the membrane deformation through enhanced hydration and the contact area between the membrane and electrode.

4. Summary

BES studies have used different reactor configurations and operating conditions (e.g. BES architecture, types of electrodes, substrate type, dominant ARB, etc.). This diverse approach makes it very difficult to objectively evaluate membrane functions on BES performance on an equivalent basis. In most cases, the performance of Nafion has been used as the baseline for comparing the feasibility of newly developed membranes for BES application. Typical parameters used for technical assessment of membranes are proton permeability, oxygen permeability, and substrate loss in MFCs, while electrode energy losses would be dominant, such as poor kinetics in the cathode. Table 1 presents a comprehensive list of oxygen mass transfer and diffusion coefficients for various membranes that have been studied for MFC application. Among various membranes, MFM, Nafion and UFM with higher molecular cutoff weights showed comparatively higher oxygen permeability during MFC operation. In contrast, other PEMs (Ultrex™CMI-7000, Selemion, and SPEEK) and AEMs showed relatively low oxygen permeability. Table 2 summarizes a list of substrate mass transfer and diffusion coefficients for various membranes. Substrate loss is usually higher for MFM, UFM with higher molecular cutoff weights might be due to presence of relatively larger pore in the membrane, and substrate loss is moderate in most of the IEMs. In MEC operation, AEMs performed better than other membranes in terms of current density and small pH gradient.

The prices of various membranes used for BES application are summarized in Table 4. From the economic perspective, Nafion membrane is the most inappropriate choice for BES application now, as the cost of other membranes studied for BES application are significantly lower than that of Nafion. Most of the reported studies used CEM or AEM, while other membranes (e.g. nanocomposite membrane) are not extensively studied yet. So far, AEM performed better than CEM for both MFC and MEC. Therefore, based on the reported studies to date, using low-cost AEM would be a good selection for large-scale BES application from both technical and economic perspectives. We found several areas that are significant for BES commercialization, but have not been studied thoroughly: (1) membrane fouling and maintenance of fouled membrane, (2) mitigating pH gradient between two chambers, and (3) transfer of oxygen molecules and value-added products from the cathode to the anode. AEM improvement that resolves

Table 4. Cost of various membranes used for BES application.

Membrane	Price ($/m^2)	References
Nafion	1400–1500	[4,35,36,43,70,85]
Ultrex (CMI-7000)	100	[84,86]
Selemion	400	[36]
AEM (AMI-7001)	80	[70]
Forward osmosis membrane	30	[86]
UFM	160–350	[43,70]
MFM	20–55	[35,43]

the three technical hurdles will facilitate large-scale BES applications.

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