

Review

A Comprehensive Study on Air-Cathode Limitations and Its Mitigation Strategies in Microbial Desalination Cell—A Review

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Abstract: Microbial desalination cells (MDCs) are promising bioelectrochemical systems for desalination using the bacteria-generated electricity from the biodegradation of organic wastes contained in the wastewater. Instead of being a sustainable and eco-friendly desalination technology, the large-scale application of MDC was limited due to the high installation cost of the metal-catalyst-coated cathode electrode and the poor performance of the cathode in long-term operation due to catalyst fouling. Such cathodic limitations have hindered its large-scale application. The cathodic limitation has arisen mainly because of three losses, such as (1) Ohmic loss, (2) mass transfer loss, and (3) activation loss. The catalyst-assisted cathodic reduction reaction is an electrochemical surface phenomenon; thereby, the cathode's surface charge transfer and thermodynamic efficiency are crucial for reaction kinetics. This review article aims to provide an overview of the MDC process, performance indicators, and summarizes the limiting factors that could hinder the process performance. Then, the article represented a comprehensive summary of the air-cathodic limitations and the mechanisms applied to improve the air-cathodic limitations in MDC to enhance the cathodic reaction kinetics through cathode surface modification through catalysts. The study is significantly different from other review studies by the precise identification and illustration of the cathodic losses and their mitigation strategies through surface modification. The details about the role of photocatalysts in the minimization of the cathode losses and improvement of the performance of MDC were well presented.

Keywords: microbial desalination cell; air-cathode; cathodic limitations; cathode surface modification



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1. Introduction

Globally, the rise of freshwater scarcity issues has become more evident due to the expanding population growth, industrialization, and climate change [1,2]. To minimize freshwater demands, different nations installed their first desalination initiatives in the late 1950s [3]. Nowadays, the number of worldwide desalination plants reached almost 16,000, where 68.7% are reverse osmosis (RO) membrane-based technology plants [3]. The conventional reverse osmosis (RO) method for desalinating saline water consumes excessive electrical and mechanical energy [4]. For instance, the energy used to purify 1 m³ of seawater is approximately 0.36–0.47 kWh [5]. Seawater desalination also uses thermal technologies, such as multieffect desalination (MED) and multistage flash (MSF). However, they have several disadvantages from a climate change perspective [6].

Recently, numerous studies have focused on developing desalination processes powered by renewable energies, such as wind, solar, geothermal, and bioenergy [7]. However, renewable energy-powered desalination processes are more expensive than conventional processes [8]. Therefore, developing a sustainable, inexpensive, and efficient desalination technology was necessary. Microbial desalination cells (MDCs) are a promising bioelectrochemical technology for desalinating seawater, requiring little or no energy (Figure 1) [9,10]. The sustainability of MDC is attributed to their use of wastewater organics as the driving

force to desalinate saline or brackish water via biological wastewater treatment and power generation [11]. Thus, integrating wastewater treatment with desalination can maximize the environmental benefits as the energy contents are extracted from the wastewater before being released into nature [12].

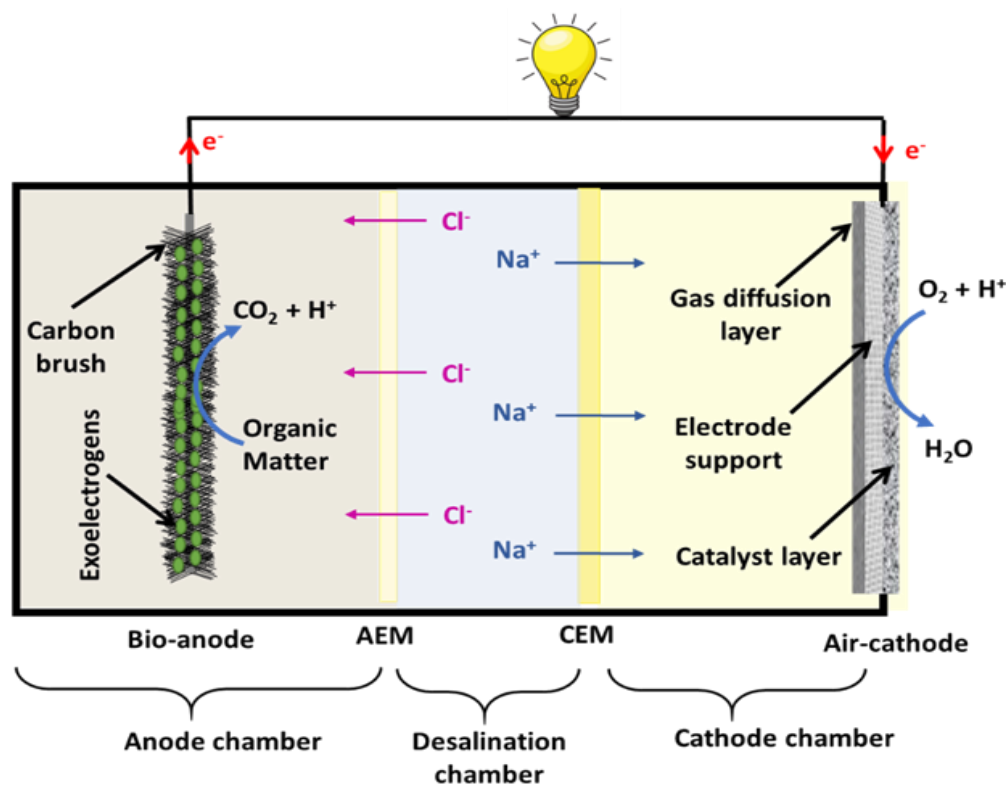
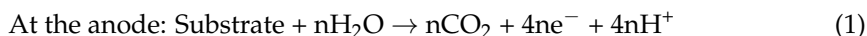


Figure 1. Schematic diagram of typical (MDC).

Many publications have been published in the last decade on various MDC reactor configurations [13–15]. Investigated reactors include biocathode MDC [16–18], air cathode MDC [8,19,20], etc. The three-chamber microbial desalination cell has been the focus of most researchers. The conventional three-chamber MDC reactors consist of anodic and cathodic chambers with a central desalination chamber separated by ion-exchange membranes [19].

The desalination mechanism in MDCs is a spontaneous process that needs no external power [20,21]. It is only dependent on the electricity produced by exoelectrogenic bacteria [22]. The organic-rich wastewater is utilized as a metabolic substrate for the exoelectrogens (e.g., *Shewanella*, *Geobacter*, etc.) that grow on the carbonaceous anode in the anode compartment [23]. The attached anodic bacteria oxidize the organic contents of wastewater by the metabolic processes that produce electrons that move to the anode by the bacterial nanowire piles, cytochrome C, etc. [9,24,25]. Then, the biogenerated electrons are sent to the cathode through an external circuit and load, where they are reduced by electron-acceptors/oxidizing-agents (e.g., O_2) present in the catholyte. Hence, a potential gradient between the electrodes is created by the electrical current flow from the bioanode to the cathode for the cathodic reaction. As a result, the ions (anions and cations) in the central compartment (desalination chamber) are forced to flow through the membranes to the surrounding chambers by the current potential. The saltwater is desalinated as a result of this phenomenon. The charge balance is maintained by ions migrating across ion exchange membranes. Through a cation exchange membrane (CEM), cations (Na^+) flow towards the cathode, whereas anions (Cl^-) migrate towards the anode, passing through the anion exchange membrane (AEM). Generally, Equations (1) and (2) represent the redox reactions in MDC [20].



For a decade, microbial desalination cell scale-up initiatives focused on desalination limitations, such as limited power output and high internal resistance caused by the MDC components [26]. Several factors, including reactor configuration, electrode materials, electrolyte conductivity, ion exchange membrane fouling, biofilm inhibition, and operational circumstances, have contributed to these limitations [14]. Electrode materials, as an illustration, affect both the MDC system performance and cost efficiency due to internal losses (e.g., electrode overpotential) [27]. High-performance electrode materials with stable structures and a large surface area must be employed in MDC to increase the power-output performance at low internal resistance [24].

Furthermore, MDC performance is influenced significantly by anodic and cathodic reactions. However, cathodic reduction is a limiting factor for stable and effective MDC performance [25]. Generally, cathodes in microbial desalination cells can be divided into cathodes submerged in liquid electrolytes and air cathodes exposed to open air [28]. Reagents are consumed as electron acceptors in the liquid-cathode MDC, which must be treated before reuse or disposal. On the other hand, air-cathode MDC uses oxygen as an electron acceptor. Thus, it can be seen as an ecofriendly and commercially scalable alternative compared to liquid-cathode MDC due to the abundance of O_2 [13]. Hence, most MDC research utilizes atmospheric oxygen as an oxidant species [29,30]. Although, limited cathodic performance was recorded due to the high overpotential of oxygen reduction reaction that reduces cathode reaction kinetics and the system's efficiency [31,32]. Accordingly, effective electrocatalysis is required to boost the oxygen reduction reaction (ORR) performance [13].

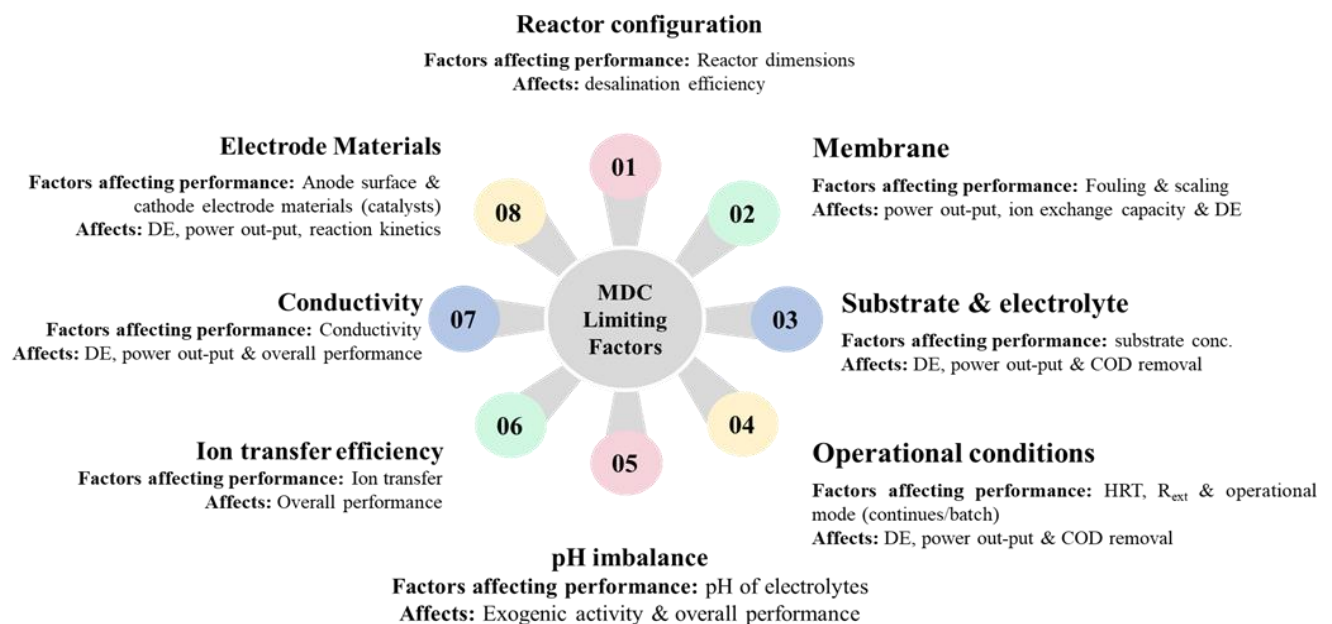
The aim of this review paper is to provide comprehensive information on the cathodic limitation and their mitigation method through a catalyst application. Several types of catalysts applied over a decade of research are reviewed, and their performance on air-cathode MDC is discussed. There is no significant review study in this area. The study of the most important parameters, i.e., cathode overpotential and cathodic losses, for efficient desalination in MDC and for industrial applications, is the novelty of this study and is well discussed. The review article will provide a new path for developing novel photocatalytic materials to overcome the negative impacts.

2. MDC Performance Indicators and Limiting Factors

The performance and efficiency of the MDCs system are indicated and measured by considering the various parameters listed in Table 1. However, any technology's overall performance and efficiency are determined and controlled by the magnitude and conditions of specific factors before, during, and after the operation [33]. The MDC system's efficiency and output are affected significantly by the configuration of the reactor constructed, including the material, dimensions, and electrode materials used. It is also influenced by the membrane (IEMS), substrate (electrolytes), and operational conditions, i.e., temperature, hydraulic retention time (HRT), and pH imbalance, as shown in Figure 2.

Table 1. MDC performance and efficiency indications.

Performance Indicator	Remarks	Mathematical Expression	References
Desalination Efficiency (DE)	Reduction percentage in saltwater's conductivity.	$DE = \frac{(\text{Salt conc.}_i - \text{Salt conc.}_f)}{(\text{Salt conc.}_i)}$	[34]
Desalination Rate (TDR)	Amount of salt removed per unit of time.	$DR = \frac{\text{Total salt removed}}{\text{Total desalination time}}$	[35]
COD Removal	The amount of organic matter removed via microbial metabolism.	$COD_{RE} = \frac{(\text{Conc.}_i - \text{Conc.}_f)}{(\text{Conc.}_i)}$	[36]
Current Efficiency	The ratio of produced current to the chamber's working volume or the number of ions separated per electron transferred at both electrodes.	$\eta_i = \frac{F_z V \Delta c}{N_{cp} \int i dt}$	[37]
Power Density	Power generation in a cell-based on the projected surface area of electrodes or electrolytes volume.	$PD = \frac{\text{Power produced}}{\text{Electrolyte's volume}}$	[38]
Coulombic Efficiency	The ratio of actual charge produced to the available charge is theoretically calculated based on the reduction in COD.	$CE = \frac{(M_{O_2} \int i dt)}{(n_e F V_{an} \Delta COD)}$	[39,40]
Ion-exchange Efficiency	The exchange efficiency of IEMs to allow the number of produced ions by anodic and cathodic reaction in MDC	-	[41]

**Figure 2.** Limiting factors of MDC performance.

Precisely, the reactor dimension, such as the volumetric ratio utilized in constructing and processing the MDC system, has shown a notable impact on its performance. Jingyu et al. (2017) revealed that a lower volume of anolyte and catholyte chambers accompanied lower reactor efficiency [33]. Cao et al. (2009) and Meng et al. (2014) used a volumetric ratio (V_{anode}:V_{cathode}:V_{desalination}) of (3:3:1) and (100:33:1) for the desalination of a 5 g/L synthetic seawater (NaCl) [41,42]. Meng et al. (2014) achieved a high desalination efficiency (DE) of 90% and a power output of 31 W/m³ compared to Cao et al. (2009), who recorded a DE of 46.37% [41,42]. In addition, constructing an MDC with a shallower-depth desalination compartment and reducing the gap between electrodes could be beneficial in overcoming the high internal resistance and optimizing the electromotive potential and power generation.

The membranes employed in MDC reactors can segregate ionic species in a solution using electrical current, resulting in a bipolar process. During reactor operation, membranes can cause the dissociation of water, which significantly reduces power output due to the loss of electrons for the dissociation process. The findings of various studies revealed that different types of membranes with high surface areas and great ion-exchange capacity could improve the removal of the salts, enhancing the desalinization efficiency by 50–63% [8,41]. However, fouling and scaling are issues that appear due to IEMs used in bioelectrochemical systems (BESs) for long-term operations, imposing extra resistance to salt removal [43].

Moreover, electrolytes have a remarkable impact on BES performance as they are considered a reservoir for ion species, a source of organic matter, and a medium for pH fluctuations [44–46]. Therefore, high salinity removal demands a large volume of electrolytes, especially anolytes [47]. In addition, the properties of substrates used to feed biofilms in an anode chamber influence the MDC efficiency. As an illustration, Kuichang et al. (2016) improved the performance of M-MDC by increasing the concentration of anolytes through adding more glucose, resulting in a maximum performance of high DE (47.3%), COD (40.2%), and a current output of 0.6 mA [48].

Further, the modes of operating MDC (batch or continuous) can significantly influence MDC stability and performance. For instance, in a batch mode, the conductivity of the electrolytes decreases with time, resulting in high internal resistance and a reduction in the overall performance [23]. In continuous mode, the reactor chambers are fed with a solution circulating continuously in cycles under specific HRT. Consider the comparative performance of UMDCs operated in batch mode and continuous mode. High performance with a maximum power density of 38 W/m³, current production (62 mA), salt removal (>99%), total dissolved-solids removal rate (7.50 g TDS·L⁻¹·d⁻¹), and efficiency of charge (98.6%) was achieved by operating UMDC under continuous mode [8]. On the contrary, Jafary et al. (2020) MDC reactor operated under batch mode recorded energy production of 8 mW, current generation (43 mA), and a desalination rate of 24.3 mg/h [11]. However, one promising future recommendation for METs is to be operated by a recirculation batch mode. Jafary et al. (2017) revealed that MFC performed in recirculation in batch mode gave a high performance of maximum power density of 38 W/m³ compared to batch and continuous modes, respectively [49].

Aside from modes of operation, hydraulic retention time plays an essential role in overall desalination efficiency. To illustrate, Jacobson et al. (2011) investigated the UMDC under HRT on days one and four using the continuous mode of operation. The results showed a maximum boost in their system's performance by increasing the HRT from 1 to 4 days. It was evident that the HRT of salt solution significantly influences the TDS since the longer hydraulic retention time allows more involvement of salt in the current generation, and thus it being removed [8].

Equally important, the external resistance (R_{ext}) is another factor that may majorly affect the MDC efficiency outputs. Numerous publications reveal that MDC performance (current production) increases by decreasing the R_{ext} [45,50,51]. A constructed upflow-stacked microbial desalination cell (USMDC) reactor operated under applied external resistance (R_{ext} , 1000 Ω –1 Ω) recorded a high desalination ratio of 91.9% when R_{ext} was

1.5 Ω [51]. The USMDC's current production increased as the R_{ext} was reduced from 500 Ω . Nevertheless, Wang et al. (2020) reported reductions in the current generation when R_{ext} continued to decrease, proving the fact that there is an optimal external resistance in which the current production can be maximized (1 Ω –5 Ω) [51]. In previous studies, the optimum external resistance values of the MDC reactors were approximately 10 Ω [52].

Furthermore, the released protons react with anions transported from the desalination chamber, producing internal biofilm acidification due to the metabolic process. As the desalination process operates over time, protons accumulate due to microbial respiration, decreasing pH in the anode compartment. Hydroxides accumulate in the cathode compartment because of oxygen reactions and rising pH values. The pH of an anode impacted the anode's potential of many METs and was the main cause of desalination efficiency reduction in MDC. Accordingly, controlling pH fluctuation has become a critical factor in optimizing the performance of BES, including MDC, especially in terms of power production and water desalination. Luo et al. (2012) introduced anolyte's continuous recirculation between a feed container and an anode compartment. This operational mode helped mitigate the anode chamber's pH reduction and raised the current output by 61% compared to results obtained under batch mode [53]. Additionally, Jafary et al. (2020) established a proof-of-concept study for a two-chamber UMDC, using a new arrangement of anion-exchange membrane and cation exchange membrane that resulted in a self-generated pH control approach [11].

To drive a desalination process in an MDC reactor, several electrons are needed to remove an equal quantity of salt from saline water. However, this number of electrons could be lost while running other reactions instead of salt removal, affecting the overall system's efficiency. The loss of electrons is caused by back diffusion and membrane resistance [33]. Further, required electrons for saltwater desalination may be influenced by other electron acceptors, such as O_2 diffusion into the anode compartment [54]. Under those circumstances, more organic oxidation reactions are needed to drive the desalination process [8]. The split of large pairs of ions due to electron transport through the systems enhances the charge transfer efficiency, improving desalination [55]. More studies on optimizing charge transfer efficiency are needed.

The concentration of ionic content in an electrolyte, which can transmit electrical charges, is referred to as conductivity, which remarkably affects MDC performance. High conductivity values resulting from high saltwater concentrations create a higher concentration gradient between chambers. If the concentration of electrolytes is lower than that of the saline water, the MDC's desalination performance is enhanced by dialysis. In addition, desalination performance is influenced by some ionic species and impurities that prohibit the overall performance. Ion transport efficiency is affected by salt solution concentration and composition. For instance, seawater contains various ions and impurities, such as Ca_2^+ , Mg_2^+ , K^+ , Br^- , SO_4^{2-} , clay, and silica, which decrease the conductivity and result in a higher internal resistance during MDC operation [56].

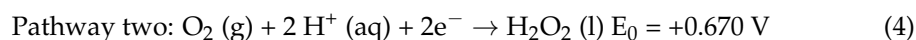
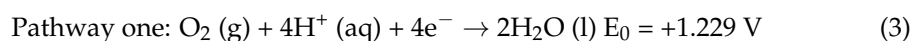
Finally, the anode surface contributes highly to the activation losses, despite the amount of gained energy by biofilm metabolism activities [57,58]. Therefore, electrodes should be created from materials with a larger surface area, so that a larger mass of biofilm can adhere to the anodic oxidation process. The adhesion of large biomass onto anode electrodes can consequently enhance the current generation [23]. Accordingly, most studies used an extensive surface area of the material. For example, carbon-based products, such as carbon felt, fiber brushes, cloths, graphite granules, graphite plates, porous graphite, activated carbon (AC), and 3D carbon nanotube (CNT) matrices [14]. However, each type of these electrodes exhibits different performances and output efficiencies because of the variations in their effective surface areas, structures, operational conditions, and metal-catalyst coatings. As an illustration, the large surface area of AC results in high electron transfer in anode compartments, as it enables microbial growth, which leads to more significant bacterial cultures [59]. In addition, AC electrodes utilized in MDC achieved a complete $\text{NH}_3\text{-N}$ removal (99%), high removal of COD (96.9%), and removal of total

PO₄ (98.3%) [60]. In comparison, applying rough surface graphite (RSG) catalysts to MDC electrodes led to a remarkably high power output of 10.8 W/m³ [61].

Cathode electrode materials also play a crucial role in retrieving electrons and in their consequent use in the reduction reaction [62]. In cathodes, the suitable terminal electron acceptors (TEA) are reduced by electrons coming from the anode, completing the cathodic half-cell reaction [63]. Further, the performance of METs significantly depends on the cathode's electron harvesting efficiency. For instance, MDC was investigated with several cathodic electron acceptors, such as oxygen, hypochlorite, permanganate, and dichromate [64]. However, cathode effectiveness is determined by TEA's reduction reaction kinetics, which is one of the critical things in microbial electrochemical technologies (MET) [65].

3. Cathodic Limitations

Depending on the final available electron acceptor source, cathodic reduction reactions can be categorized as aerobic or anaerobic reactions [66]. The terminal oxidant (electron acceptor) in aerobic cathodes is oxygen (O₂). O₂ reduction is the most prominent electrochemical reaction at the cathode's surface, and it is an excellent oxidant due to the ultimate abundance of O₂ and high redox potential [65]. During cathodic oxygen reduction, two processes may take place (Equations (3) and (4)) [65].



The incomplete reduction in O₂ lowers energy conservation efficiency and produces free radical species with reactive intermediates, which can be destructive. Anaerobic conditions can also be maintained in the cathode compartment as microorganisms transport electrons from the cathode to the final oxidant (electron acceptor, e.g., nitrate). As long as the substrate is provided, an ideal BES technology can produce power simultaneously with a sustained steady voltage [65].

Practically, because of the irreversible losses (overpotentials), the predicted ideal voltage of a BES is higher than the actual voltage output. Figure 3 depicts the typical power-current curve (Figure 3b) and compares it to the theoretical and actual voltages with the parasitic losses (occurred due to undesired reactions) and the cathodic activation, Ohmic, and concentration losses, considered as the three significant overpotentials affecting MDC performance (Figure 3a). These irreversible overpotentials can be the required voltage to compensate for the current loss caused by electrochemical reactions, charge transport, and mass transfer processes in the cathode and anode chambers. The magnitude of these overpotentials varies and differs depending on the system. The real operational voltage output (V_{op}) of a BES can be calculated by subtracting the voltage overpotentials associated with each chamber from the thermodynamically predicted voltage (E_{thermo}) [65].

$$V_{op} = E_{thermo} - [(\eta_{act} + \eta_{ohmic} + \eta_{conc})_{cathode} + (\eta_{act} + \eta_{ohmic} + \eta_{conc})_{anode}] \quad (5)$$

where η_{act} refers to the activation overpotential caused by reaction kinetics, η_{ohmic} represents the Ohmic overpotential from internal resistances, and η_{conc} is the concentration overpotential attributed to mass transport implications. The equation above illustrates that cathode and anode overpotentials collectively limit the BES's overall performance. Notably, the performance of MDC can be optimized by improving both electrodes. However, this section aims to illustrate and review the cathodic limitation of bioelectrochemical systems, such as MDC (Figure 3).

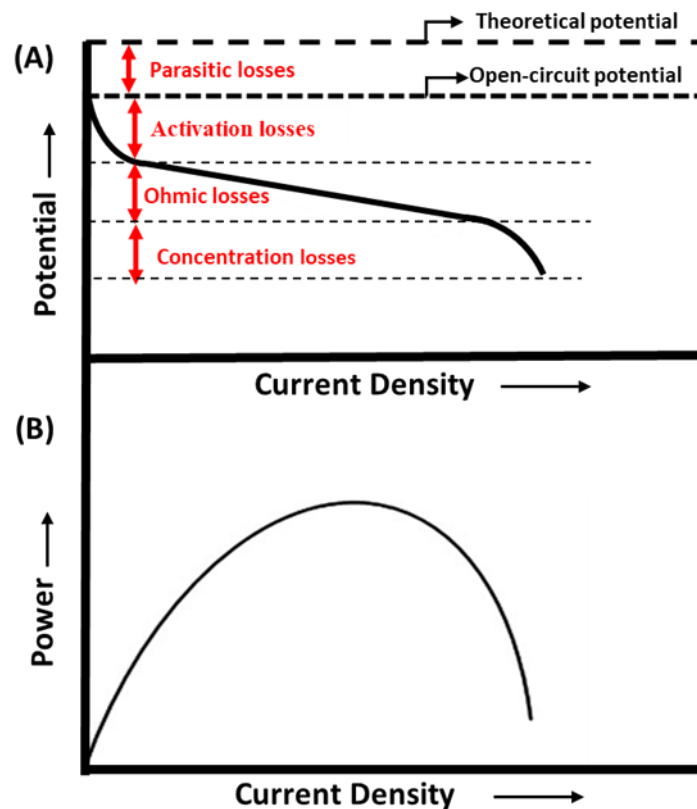


Figure 3. (A) Different types of cathodic overpotentials, (B) Power-current curve.

3.1. Ohmic Losses

In general, Ohmic losses are caused by the internal resistance of electrodes, electrolytes, and membranes. The performance of MDC is restricted by the cathodic Ohmic losses known as internal resistance. This loss is the voltage demanded to drive processes of electrons and proton transport. Since the conductors in MDC are not ideal, they intrinsically resist the charge flow. Therefore, the Ohmic loss (η_{ohmic}) indicates the voltage lost to achieve charge transport (i.e., electrons and protons) (Equation (6)). The Ohmic overpotential generally follows Ohm's law [65].

$$\eta_{ohmic} = iR_{ohmic} \quad (6)$$

where i represents the current (A) and R_{ohmic} is the Ohmic resistance (Ω) of the BES. Usually, the internal resistance is dominated by the resistance to ions and electron flow. Thus, the cathodic Ohmic resistance combines both ionic (R_{ion}) and electronic (R_{elec}) resistances, including resistances from electrodes, electrolytes, and interconnections (Equation (7)) [65];

$$R_{ohmic} = R_{ion} + R_{elec} \quad (7)$$

Since ionic conductivity is an order of magnitude lower than the electrical conductivity of electrode materials, the electrolyte resistance dominates the internal resistance (i). The electrolyte Ohmic resistance (R_{ion}) can be represented as shown in Equation (8) [65];

$$R_{ion} = \frac{l}{AK} \quad (8)$$

At medium current densities, the cathodic Ohmic losses are more pronounced, where according to Ohm's law, the operating voltage drops linearly as the current rises. Hence, improving the performance of MDC requires lowering the cathodic Ohmic losses. Many have been published on Ohmic losses, including the first proof-of-concept MDC by Cao et al. (2009). They noticed a high internal (Ohmic) resistance increase from 25Ω – 970Ω after

achieving a 88% salt removal of a 5 g/L NaCl [41]. In addition, Chen et al. (2011) reported lower current and desalination efficiencies associated with a high Ohmic resistance (21 Ω –312 Ω) while desalinating 20 g/L of NaCl [52]. Kokabian and Gude et al. (2015) illustrated that Ohmic overpotentials dominate voltages, affecting system performance [39].

3.2. Activation Losses

The current production of MDC is mainly controlled by the kinetics of the reduction reaction occurring at cathodes. However, the energy barrier (activation barrier) hinders the reduction of oxidants, which limits the reaction kinetics. A part of the cathode potential is lost when current is drawn from the system to overcome this activation barrier. This lost portion of cathode potential is called cathodic activation overpotential (η_{act}) cathode (activation loss) [65].

At low current densities, the activation overpotential leads to exponential loss on the current-voltage curve, as shown in Figure 3. As more electrical current is taken from a BES, the activation overpotential increases, leading to a lower cell potential. Further, a BES technology's efficiency output and performance are dominated by the cathodic activation overpotential. However, the extent of cathodic activation loss depends on the kinetics of the reduction reaction. Kinetics can be boosted by reducing the activation energy barrier and increasing the temperature, interface area, or oxidant concentration [65].

3.3. Mass Transport Losses

The mass transfer usually governs the process of supplying oxidants (electron acceptors, e.g., O_2) and removing products (H_2O) from MDC cathodes. In cathode compartments, this loss is caused by the significant discrepancies between reduced and oxidized species present in both the cathode surface and solution. Moreover, insufficient or incomplete mass transport leads to reactant depletion and product accumulation. The lack of reactants leads to a performance loss caused by affecting both the cell voltage and reaction rates. This loss of concentration (mass transport overpotential) can be defined as the amount of voltage needed to achieve the mass transport at the cathode (η_{conc}) cathode. Additionally, concentration losses can take place at high densities of an electrical current and increase as the electrical current densities increase (Figure 3). It must be noted that mass transport limitations due to oxidant transport in the cathode chamber are typically more severe than those in the anode chamber. Henceforth, only the oxidant limiting concentration is considered in determining the mass-transport losses in a BES [65].

3.4. Other Losses

The parasitic losses, such as substrate crossover and side-reactions occurring in the cathode chamber, collectively affect the MDC operational efficiency. For instance, the substrate crossover through membranes from the anode chamber to the cathode compartment has been illustrated in several MFCs. Ideally speaking, membranes should prevent reactants from transporting between the anode and cathode compartments. However, substrate crossover is commonly caused by electro-osmosis and molecular diffusion. This reactant crossover is more severe in membrane-less BES since there is no physical barrier to separate the contents of the anode and cathode chambers [62].

Furthermore, substrate crossover affects the cathodic performance by reducing the potential to lower than the thermodynamically predicted values. It also influences the coulombic efficiency as the substrate is used or transported from the anode compartment. Moreover, the oxidation products of the substrate may cause some structural changes in the cathode's surface area and poison the cathode catalyst. The impact of reactant crossover on cathode overpotentials might be influenced by a variety of parameters, including reactant concentration, membrane material and thickness, electrode material and spacing, and the current output [65].

Several approaches reduce the substrate crossover and other cathodic overpotentials of activations, concentrations, and Ohmic losses. These approaches include reducing the

substrate concentration, increasing the current density, improving membrane materials, designing electrodes, and finally, cathode catalysts, which are discussed in the following section [65].

4. Cathode Surface Modification

Oxygen reduction is the most common reaction in MDC cathodes [63]. Although, the high reduction overpotential caused by the slow rate of O_2 reduction on the surface of the cathode electrode (e.g., graphite/carbon) is one of the main limiting factors in MDC performance [65]. Thus, enhanced cathodic reaction rates influence the performance of MDCs and constitute significant challenges for research and development. Several approaches were explored in numerous studies to enhance and improve the overall performance of cathodes by reducing the cathodic overpotential for O_2 . The employment of mediators, electrode modifications with electro and photo-catalysts, and improving the operational conditions inside the cathodic chamber are all examples of these approaches [65].

Moreover, a cathodic reduction reaction is an electrochemical surface phenomenon. Hence, the surface of the cathodic electrode is crucial in the reduction reaction kinetics of O_2 . Notably, pure or plain carbon/graphite electrodes are associated with nondurable and ineffective ORR due to their lower electrochemical activity. Therefore, it was essential to coat cathodes with a catalyst layer [67,68]. Usually, cathodic reactions occur at the three-phase interface of air, electrolyte, and catalytic material. Thus, cathodes in MDC consist of three main layers: the diffusion layer (DL), conductive support material layer, and catalyst layer (Figure 4). However, the path in which the ORR can follow (direct four-electron or two-electron process) is strongly controlled by the type of catalyst used. This section will focus on MDC's air-cathode surface modification by applying different abiotic catalysts to optimize the ORR performance.

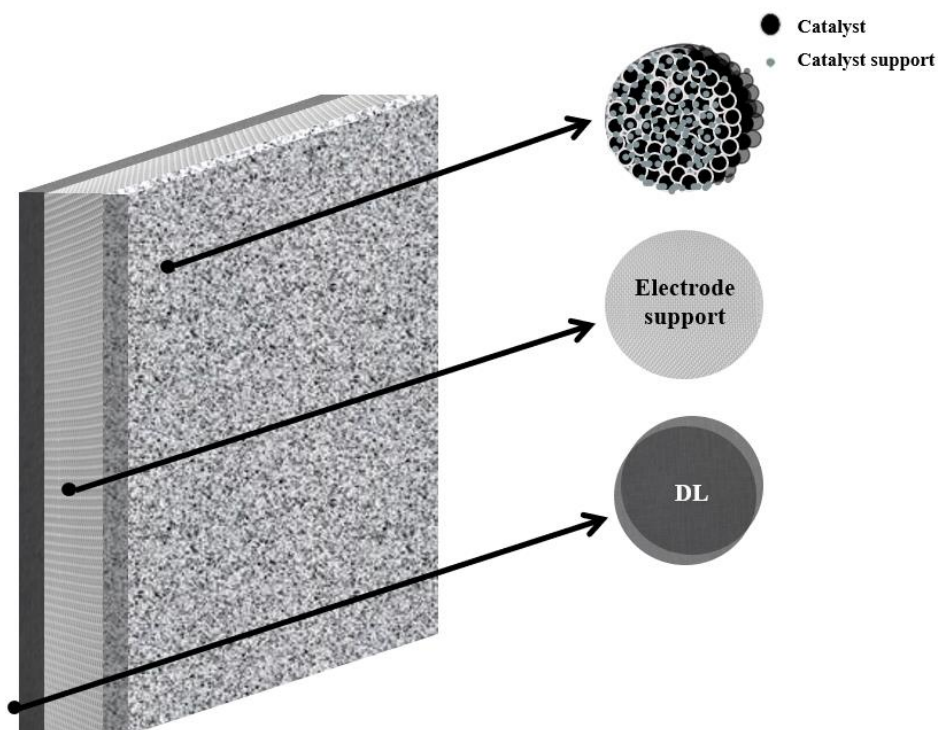


Figure 4. Cathodic surface layers (DL-diffusion layer).

By using the Scopus database (www.scopus.com) utilizing “MDC” as the search keyword, more than 190 articles were published over the span of 11 years (2010–2021) (Figure 5). Further, the search was narrowed by focusing only on air-cathode microbial desalination cells. Thus, through the utilization of “air-cathode” and “air-cathode microbial

desalination cell” as keywords, 38 articles published from 2010 to 2021 were screened and analyzed for relevant information on the type of applied cathodic catalysts on the MDC technology (Table 2).

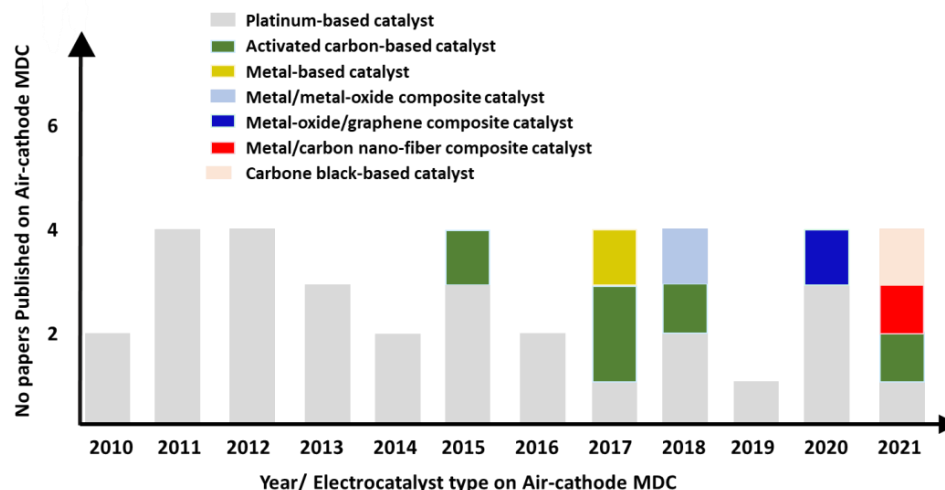


Figure 5. Number of research papers on air cathode MDC (2010–2021).

For an optimal ORR to occur, the catalyst should have high catalytic activity, stability, durability, high poisoning resistance, and cost-effectiveness. The catalyst’s performance in boosting ORR reactions depends on the catalyst’s surface area, morphology, conductivity, and the interaction between electrode and catalyst materials [69]. In addition, the effective catalyst should be capable of performing the direct four-electron reduction reaction. Scientists have found that synthesized noble metals, such as Pt, dominantly follow the direct 4^-e reduction process [70].

Platinum (Pt) has been globally utilized as the most effective catalyst due to its relatively large surface area and favorably low ORR overpotential. Logan et al. (2005) reported higher power outputs of an MFC while using a Pt-coated cathode than a plain carbon cathode [71]. Significant reductions in salt concentration and COD with high power density were achieved in air-cathode MDCs with a Pt catalyst in comparison to the first developed MDC reactor by Cao et al. (2009) [19,44,72–74]. Despite the excellent catalytic properties of Pt, the high cost of this catalyst prevents it from being utilized in large-scale applications. The quantity of Pt load needed for coating cathode electrodes has been reduced in an attempt to address this issue. Cheng et al. (2005) utilized a low Pt load (0.1 mg/cm^2) and observed no significant reductions in MFC performance [75]. On the contrary, Maskarenj et al. (2015) showed that using low Pt loads to achieve cost-effectiveness affects the MDC performance by raising the internal resistance [76,77]. However, a platinum-based catalyst’s pH sensitivity and toxicity make it unsuitable for real-life applications [78].

Consequently, efforts were directed towards enhancing ORR using Pt-free, inexpensive catalysts. As an illustration, the carbonous materials, i.e., activated carbon (AC), carbon black (CB), graphene, graphite, carbon nanotubes (CNTs), and carbon nanofibers (CNFs), are found in abundance with high electrochemical surface areas. For instance, the thermally produced AC was introduced into air-cathode MDC for the first time in 2015 because of its high surface area ($>600\text{--}800 \text{ m}^2/\text{g}$) and low cost [78]. Although AC-based catalysts exhibit lower performance attributed to their low electronic conductivity. Thus, a blending strategy of AC with other conducting carbon-based materials, such as CB, was adopted to enhance the conductivity of this catalyst. Due to the synergistic effect of the AC/CB composite, the blending strategy has contributed to the high catalytic activity of AC towards ORR [79]. For example, Santoro et al. (2017), Moruno et al. (2018), and Moruno and Rubio et al. (2018) recorded high desalination efficiencies ranging between 50 and 70% using an AC/CB catalyst [80–82]. It is worth mentioning that different parameters have been attributed to

the high desalination performance in these studies, including the type of membrane used and operational conditions.

Table 2. Electrocatalyst applied on air-cathode MDC Systems.

Air-Cathode Catalyst	Load (mg/cm ²)	Cathode	Type of MDC	Max. Power Output	MDC Performance			Anode	Reference
					DE _{max} %	COD%	CE%		
Precious metal-based electrocatalysts on Air-cathode MDC									
Pt/C	-	-	3-C MDC	0.42 W/m ²	43	77	68	CC	[19]
Pt/C	0.5	CC	3-C MDC	1.4 A/m ²	~68	~38	~48	CC	[72]
Pt	0.5	CC	5-C SMDC	7.4 mA	99	-	-	CF	[52]
Pt/C	0.5	-	5-C SMDC	1.14 W/m ²	98	91	80	GFB	[83]
Pt	0.5	CC	3-C MDC	0.66 A/m ²	24	25	-	GB	[84]
Pt	0.5	CC	5-C cSMDC	5.9 A/m ²	65	~64	~30	GR	[85]
Pt/C	0.35	CC	3-C MDC	9.3 W/m ²	39	79	25	CFB	[73]
Pt/C	0.5	CC	Multi-A MDC	6850 W/m ²	~26.0	~62.8	84	CFB	[86]
Pt/C	0.5	CC	3-C MDC	1980 W/m ²	~97	~60	~35	CGFB	[87]
Pt/C	0.5	CC	MEDIC	0.65 W/m ²	~40	~78	~54	GFB	[88]
Pt/C	0.5	CC	7-C SMEDIC	~0.65 W/m ²	94	~88	61	GFB	[89]
Pt/C	0.5	CC	3-C MDC	28.6 mA	-	-	-	GAC	[44]
Pt/C	0.5	CC	5-C SMDC	-	36	-	-	CGFB	[34]
Pt	0.5	CC	3-C MDC	-	91(Na ⁺)	-	-	CB	[56]
Pt	0.5	CC	7-C USMDC	32.91 W/m ³	96	-	-	CF	[51]
Pt	0.5	CC	5-C QMDC	17.18 mW	48.12 (mg/h)	-	-	CFB	[50]
Pt	0.5	CC	2-C UMDC	8 mW	85	24.3 (mg/h)	84	CFB	[11]
Pt	0.5	CC	3-C MDC	4.54 mA	>99	51.74	88.67	CB	[74]
Pt/C	0.4	CC	Pt/C 2-C UMDC	30.8 W/m ³	99	-	-	GG	[8]
Pt/C	0.4	CC	2-C UMDC	28.9 W/m ³	94	-	92	GG	[90]
Pt/C	0.5	CC	4-C SMDC	2.5 mA	70	-	-	-	[91]
Pt/C	0.2	CC	2-C UMDC	11 mA	100	-	-	CFB	[92]
Pt/C	0.2	CC	2-C UMDC	~12.3 A/m ³	~88.1	70	5–10	CFB	[93]
Pt/C	0.1	CC	2-C UMDC-FO	-	99.4	93	~83.6	CB	[94]
Pt/C	0.5	CC	3-C MCDC	-	70	-	-	CFB	[95]
Pt/C	0.1	CC	2-C UMDC-FO	32.9 mA	94	70.6	83.6	CB	[94]
Pt/C	0.4	CC	2-C UMDC	300 A/m ³	~80	~80	~80	GG	[96]
Pt/C	5	CC	Flow backwater	1929 W/m ²	-	68.9	-	CB	[97]
Metal-oxides and their composites									
Ag/SnO ₂	0.05 (Ag-NPs), 1 (SnO ₂)	CF	5-C MDC	1.47 W/m ³	72.6	-	~14.4	-	[98]
MnO ₂	1–2	CP	3-C MDC	41 A/m ²	56.30	1.16 (kg/m ³ /d)	31.59	CF	[13]
Activated carbon (AC)-based									
AC	5	CC	2-C UMDC-AD	2000 mA	42	96	15.5	CB	[78]
AC	-	CC	5-C MEDCC	~32.8 A/m ² ,	~39.7 (mg/h)	-	~105	CB	[99]
AC/CB	40	-	3-C MDC	~3.01 W/m ²	>60	94	-	CB	[100]
AC/CB	40	SSM	3-C MDC	~2350 W/m ²	~78.6	-	-	CB	[81]
AC/CB	40	SSM	3-C MDC	~1890 W/m ²	~53	-	-	CB	[82]
AC/CB	-	SSM	3-C PMDC	340 W/m ²	~83.4	-	-	CFB	[101]
Carbon black (CB) composites									
PMo/CB	25	CC	Flow backwater	3372 W/m ²	-	>90	-	CB	[97]
CB	-	CC	Flow backwater	1627 W/m ²	-	32.7	-	CB	[97]
Nonprecious M–N–C									
Fe–N–C	0.1–0.4	-	3C MDC	~49 W/m ²	46–55 %	73–83%	39 ± 7%	-	[100]
Graphene composite									
MnO ₂ /graphene	-	CC	3-C MDC	125 W/m ²	~15.7	~85.1	~1.52	CC	[30]
CNF									
Fe/CNF	-	CF	3-C MDC	13 A/m ²	48.33	1.14 (kg/m ³ /d)	13.11	CF	[13]

Despite the good records associated with the carbonous materials applied in MDC, their lower performance than Pt-catalysts impedes their real-life application. Other ma-

materials should be investigated to improve the ORR similarly to Pt, but have lower prices. Transition metals, metal-oxides, and their composites with metal-N-C complex catalysts are all examples of Pt-free materials that exhibit phenomenal output efficiencies in air-cathode microbial desalination cells (MDC).

The ball milling of the synthesized MnO_2 catalyst by Aliaguilla et al. (2021) in a 3-chamber MDC exhibited good desalination performance (56.30%) under negative potentials [13]. This result was attributed to the excellent morphological and electrochemical characteristics of MnO_2 . This catalyst's perfect crystallinity and good electronic conductivity under high overpotential led to a significant reductive current density. The high current density is derived from the large absorbance of O_2 , consequently enhancing the ORR and desalination efficiency [13]. Interestingly, Aliaguilla et al. 2021 revealed that MnO_2 contributed to the high overall performance with low internal resistance and showed better catalytic activity than Pt/C [13].

Different researchers doped the transition metals with metal oxides to enhance the MDC performance to create a metal/metal-oxide composite catalyst. For example, the hydrothermally produced silver nanoparticles doped with the sol-gel-synthesized tin dioxide (Ag/SnO_2) illustrated a high desalination efficiency of 72.6% [98]. The recorded results were due to the excellent catalytic activity of Ag/SnO_2 caused by the increased surface area and electronic conductivity that enhanced O_2 absorption and reduction, leading to significant ORR [98].

Other studies investigated metal-oxides doped with a carbon-based material to enhance their catalytic performance. As an illustration, Elawwad et al. (2020) utilized the MnO_2 anchored into graphene nanosheets to produce an MnO_2/G catalyst applied to a three-chamber air-cathode MDC. The used cathodic material was synthesized through a mediated simple approach instead of the Hammer method used by several pieces of literature involving highly toxicological chemicals. The catalyst showed superior catalytic activity and stability, resulting in a high current and power output. Unfortunately, MnO_2/G exhibited lower desalination performance than Pt-group catalyst [30].

Notably, the metal oxides were not only doped with carbon-based material, but also the nonprecious metals, such as Fe, Co, and ext. Aliaguilla et al. (2021) investigated the MDC performance using an iron-doped carbon nanofiber (CNF/Fe) that showed a DE of 48.33% under positive voltages because of this catalyst's catalytic characteristics were revealed in electrochemical and morphological tests [13]. However, in the last four years, a new class of complex catalysts has been developed and applied to MET cathodes called metal-nitrogen-carbon catalysts. Santoro et al. (2017) prepared a Fe-N-C catalyst using the sacrificial support method. The new complex catalyst had higher electrocatalytic activity than Pt and AC catalysts (tested coincidentally with Fe-N-C) even when it lost 1.5% of its initial performance [100].

Similar to those applied on MFC cathodes, other catalysts may be used in MDC. Coupling the photocatalysis and electrocatalysis to synthesize a photo-electrocatalyst that can be excited by ultraviolet or visible light to enhance the ORR and desalination performance is recommended. Several studies examined the viability of the photo-electrocatalyst on MFC; scientists have demonstrated the utilization of different photo-electrocatalysts excited by visible light, such as Bi/TiO_2 [77], CuO/ZnO [102], and Pd-SiNW [103]. The performance of MFC was enhanced using these types of cathodic photocatalysts. However, in MDC, the application of photo-electrocatalyst on the cathode surface has not been investigated yet. The only study was by Liang et al. (2016), who synthesized and utilized a photo nanostructured $\alpha\text{-Fe}_2\text{O}_3$ electrocatalyst on MDC's anode, improving overall performance [104]. Therefore, applying such a catalyst to the cathode will be exciting research to conduct and undertake, especially regarding using visible light to exit the photo-electrocatalyst.

5. Conclusions

With significant performance improvement, the newly developed MDC technology could be a sustainable and eco-friendly alternative to energy-intensive desalination. How-

ever, the MDC technology is still in the development stage due to a number of issues that have to be resolved before scale-up and industrial application. The results of the study identified that the cathodic surface reaction's overpotentials and cathodic losses were the major limitations for the poor performance of the MDC technology. The study also found that a broad type of electrocatalyst could be utilized on the MDC air-cathode to optimize the ORR and enhance the desalination performance. Metals and metal-oxides-based electrocatalysts showed great potential in eliminating Pt-based catalysts on the carbon electrode. Nevertheless, the electrocatalysts used on the cathodic surfaces of different MDC configurations did not exhibit adequate enhanced performance to bring MDC into a large-scale application. Therefore, the cathode surface can be improved and modified using different approaches, mainly applying catalysts, catalyst-binders, and in-situ air abrasion applications to control catalyst fouling.

Other than those losses, there are many factors which limit the MDC's performance, such as substrate conductivity and external resistance. More discussion on these parameters and the latest technology needed to make this MDC process sustainable is needed. To improve ORR and desalination performance, it is advised to combine photocatalysis and electrocatalysis to create a photoelectrocatalyst that can be stimulated by UV or visible light. However, in MDC, the application of a photoelectrocatalyst on a cathode surface has not been investigated yet. Therefore, the application of such a catalyst on the cathode will be an interesting research project to conduct and undertake, especially in respect of using visible light to exit the photoelectrocatalyst.

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