Review

Cathode Material Development in the Past Decade for H_2 Production from Microbial Electrolysis Cells

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ABSTRACT: Cathode materials are critical for microbial electrolysis cell (MEC) development and its contribution to achieving a circular hydrogen economy. There are numerous reports on the progress in MEC cathode development during the past decade, but a comprehensive review on the quantitative comparisons and critical assessments of these works is lacking. This Review summarizes and analyzes the published literature on MEC cathode and catalyst development in the past decade, providing an overview of new materials examined during this time period and quantitative analyses on system performance and trends in materials development. Collected data indicate that hybrid materials have become the most popular catalyst candidate while nickel materials also attract increasing interest and exploration. However, the dilemma between higher H_2 production rate and larger MEC volume remains and still requires more investigation of novel MEC cathode catalysts and configurations to offer a solution.

KEYWORDS: Bioelectrochemical system, Microbial electrochemical technology, Cathode catalyst, Hydrogen, MEC, Microbial electrolysis cell, Wastewater
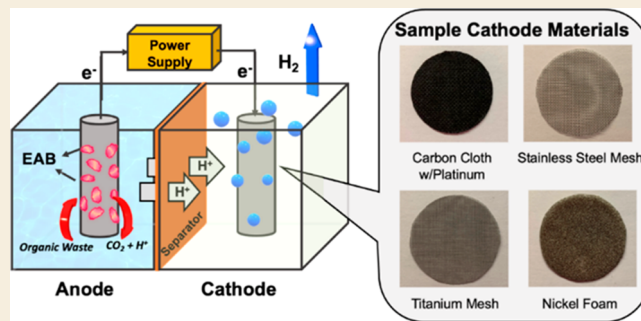
1. INTRODUCTION

The transition from fossil fuel energy to renewables is demanding the fast development of energy storage and transmission systems. H_2 will play a major role in this process due to its complementary nature to renewable electricity as a clean fuel and energy carrier as well as an energy storage medium. H_2 is one of the most essential chemical building blocks for many industries.[1,2] H_2 is increasingly produced by water electrolysis powered by renewable energy sources such as solar or wind compared to traditional natural gas reforming. Microbial electrolysis cells (MECs) carry a unique benefit in this context as they demonstrate good potential to convert biomass and waste organics into high quality H_2 while concurrently solving environmental challenges such as wastewater treatment.[3−5]

MECs employ electroactive bacteria in the anodic chamber to oxidize substrates and generate an electrical current, which is directly used to assist proton reduction in the cathodic chamber and reduce external voltage needed for H_2 evolution (Figure 1).[6−8] Compared to abiotic water splitting that requires ∼1.8−2.0 V to overcome the thermodynamic barrier, MEC leverages the chemical energy in organic compounds. As a result, much less external voltage (∼0.6−1.0 V) is required, and even such a small voltage need can be met when the traditional cathode is replaced with a photocathode or by deploying an *in situ* power management circuit.[9,10]

While a MEC shares the same reaction mechanisms with other microbial electrochemical systems, the cathode material has been known as the critical factor in determining the H_2 production rate and yield as well as the cost and scalability for real-world applications.[3] An ideal catalytic cathode in a MEC should possess several properties such as high conductivity, large surface area, high stability, low cost, and high catalytic efficiency. While carbon has been the primary base material, platinum (Pt) catalyst has been a long-time benchmark catalyst that has been gradually replaced by lower-cost catalysts or composites due to its high cost and vulnerability to poisoning.[4,11,12] In the past decade, several studies discussed MEC cathode catalyst developments and provided good insights,[13,14] but there lacks a comprehensive study that contains quantitative comparisons and analyses of performance measurements, since it has been nearly a decade when the last comprehensive review was conducted on this subject.[15]

With the MEC technology moving quickly from lab research to field applications, this Review aims to capture recent MEC
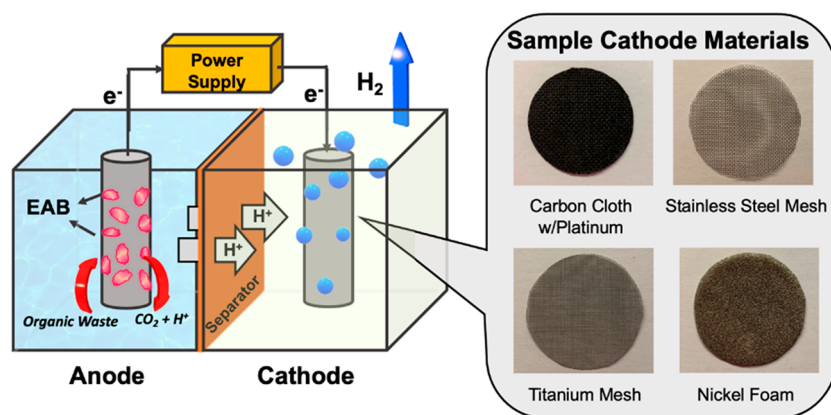
Figure 1. Reaction mechanisms of a typical two-chamber microbial electrolysis cell and common cathode materials.
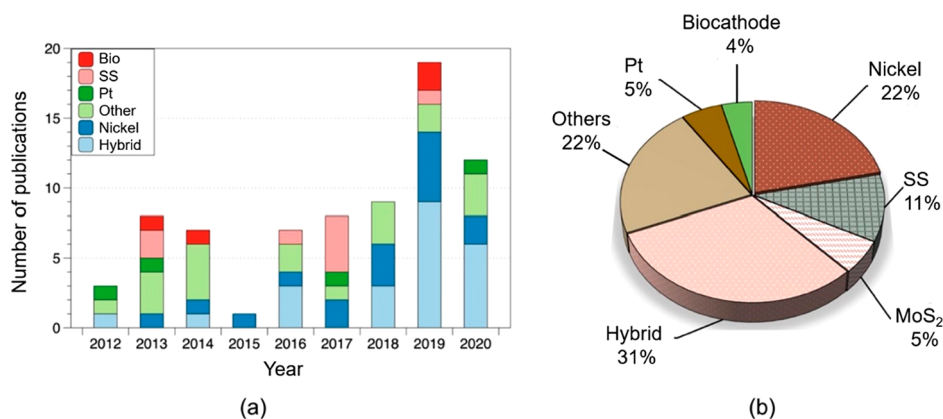

Figure 2. Summary of microbial electrolysis cell catalysts used in novel material studies from 2012 to 2020. (a) MEC cathode studies by year; (b) proportion of cathode catalyst materials experimented.

cathode advancement and provide an updated and critical assessment for optimal development. This Review focuses on MEC studies that specifically evaluate novel cathode catalysts and does not cover MEC studies with other purposes such as substrate and scale-up examinations. Pt catalyst performance data are only included when Pt is examined other than the naïve Pt/CC, and these studies are categorized separately under Pt due to the unique significance of Pt. Finally, this Review provides a summary on the important development trends of MEC cathode materials and an outlook into possible future research directions in this rapidly evolving and dynamic field.

2. DEVELOPMENT OF MEC CATHODE CATALYSTS IN THE PAST DECADE

In this Review, MEC cathode catalysts are mainly categorized into Pt, nickel (Ni), stainless steel (SS), hybrid materials, biocathodes and others based on the literature. We define the hybrid materials as the mixes of metals, carbon, organics and other materials, such as alloy, carbon–metal hybrids.[16] Stainless steel, a popular alloy for cathode catalyst, is not classified as a hybrid material for discussing cathode catalysts comprehensively in this study, but it does contain multiple elements, such as Ni, chromium, etc.[15]

Rapid development of cathode catalysts in MECs has been observed in the past decade (Figure 2). Notably, a clear shift is seen from a single catalyst being replaced by hybrid materials, which provide a combination of catalysts for improved

structural and electrochemical properties. Figure 2a shows the breakdown of MEC cathode catalysts by year. We can see that MEC catalysts studies remain popular, with a general increase in published article numbers and materials. Figure 2b shows the proportion of MEC cathode catalyst materials used for experiments since 2012. Though discovered more than a decade ago, nickel remains the most popular individual material at 22%. On the other hand, stainless steel represents 11% of all studies while Pt has usually been used as a control material. We see hybrid and other materials serving as the two largest contributors at 31 and 22%, respectively. Most hybrid materials, such as MoS_2, are complements to main materials Ni or SS to enhance their performances. Biocathode represents a relatively small portion of MEC cathode studies, which remained tepid since 2012.

When discussing MEC cathodes, we make the subtle distinction between the cathode base and the catalyst. Usually, the cathode base (e.g., carbon cloth, nickel foam, etc.) is used for supporting the reactor structure and conducting electrons,[14] for example, Pt as the catalyst and carbon cloth (CC) as the base cathode in the case of Pt/CC. Some researchers demonstrated that single material cathodes can be competitive[17−19] and possess the advantage of being easy to manufacture, which is important for MEC scale-up. In this Review, we consider single material cathodes with catalysts that can catalyze the hydrogen evolution reaction (HER) without the addition of a separate base material. Compared to MEC studies until 2012, we found that single material cathodes drastically decreased in popularity and were replaced
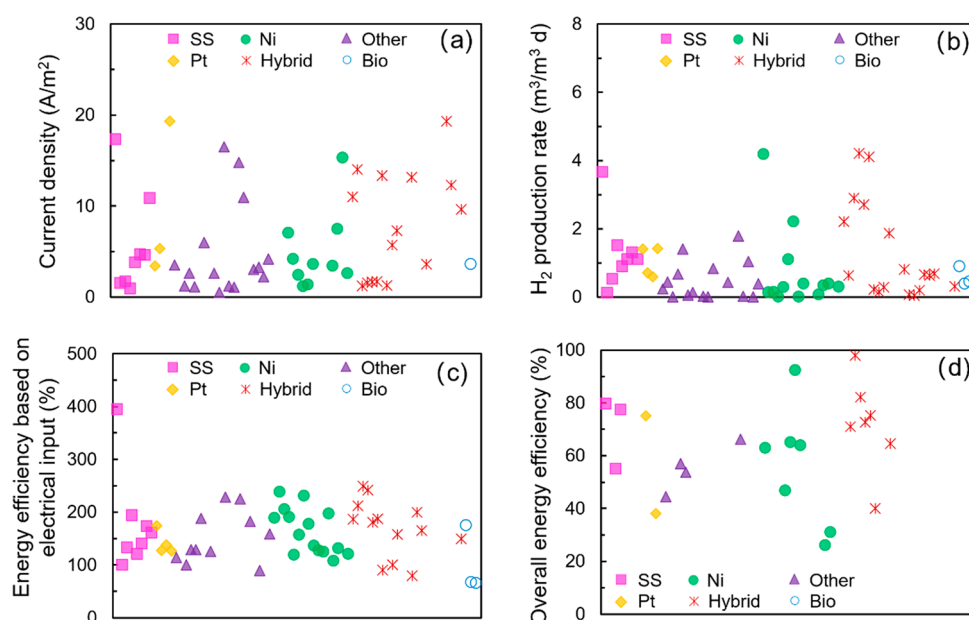
Figure 3. Performance comparison of MEC cathodes in novel catalyst studies, categorized by material type. (a) Current density; (b) hydrogen production rate; (c) energy efficiency based on electrical input; (d) overall energy efficiency.

by competitive hybrid catalyst cathodes.[15] For the base materials, the rise of nickel foam (NF) is a significant trend; this material quickly gained popularity since its introduction in 2010[20] and is the most popular base material in our collected studies. When using nickel foam as the base to coat the Pt catalyst, Pt/NF outperformed Pt/CC, exhibiting its compatibility and potential as a base electrode with other catalysts.[21] The increased popularity in NF shows its maturity and promise as the next standard as a MEC base material. Stainless steel (SS), on the other hand, despite being introduced around the same time as NF, is rarely used to experiment with. Although base materials contribute to HER in MECs, the catalysts have been proven to be crucial components in realizing highly efficient H$_2$ production in MECs. Thus, focus and interest had been drawn to improving catalytic properties and overall reaction kinetics for the catalysts beyond the base materials.

3. MEC PERFORMANCE COMPARISONS WITH DIFFERENT CATHODE CATALYST MATERIALS

3.1. H$_2$ Production

To analyze the development of MEC cathode catalyst materials comprehensively, Figure 3 summarizes four key MEC performance measurements to compare between the six catalyst categories. Figure 3a and b illustrates two metrics, current density and H$_2$ production rate, which directly reflect the distributions of H$_2$ production from MECs with various cathode catalysts. In Figure 3a, the highest current densities, ~19.3 A/m^2, were achieved in the studies exploiting cathodes of Pt/carbon nanotube as well as NiO/MoO$_2$/MoO$_3$/C composite.[22,23] Most studies produced current densities lower than 10 A/m^2, stating that current density is also restricted by other factors, such as bioanode, substrate, configuration, etc.

Figure 3b compares the H$_2$ production recovery rates (HPRs) among all reported MEC cathodes by catalyst and by year. HPR is one of the important indicators of MEC performance, indicating the volume of H$_2$ produced per MEC reactor volume during a period of time.[3] The theoretically

maximum HPR (Q_{max}) should be directly proportional to the current density:

$$Q_{max} = \frac{43.2 I_v r_{cat}}{F c_g(T)} \tag{1}$$

where I_v, r_{cat}, and $c_g(T)$ represent the average current over a time period, cathodic hydrogen recovery, and molar density of gas at standard temperature and pressure. F is the Faraday constant, = 9.65×10^4 C/mol.[25−28]

Compared to Figure 3a, Figure 3b shows that the distribution of HPR is bottom heavy, meaning that most experiments reported similar H$_2$ production recoveries. The highest HPR of 4.2 m^3/m^3 day using these new types of catalysts was lower than the absolute maximum rates that Pt and Ni foam achieved in the previous decade (between 17.8 and 50 m^3/m^3 day),[20,29,30] yet in controlled studies novel materials are insufficiently competitive. Since the focus of the Review is on new types of catalysts and materials, the traditional Pt based studies were not included unless they were used as a comparison in the same study. The distribution is also bottom heavy and ranges from ~0 to 4.1 m^3/m^3 day.[15] The highest HPR for all studies conducted specifically to examine novel catalysts of 4.2 m^3/m^3 day using Ni−Co−P is higher than that of the Ni−Co catalyst (2.9 m^3/m^3 day) and Ni catalyst (2.2 m^3/m^3 day) and demonstrated the advantage of including Co and P.[31] Electroformed Ni mesh is a single material cathode with the highest HPR of 4.2 m^3/m^3 day and is competitive to the Pt/CC control cathode.[17] Another study utilized a hybrid material cathode of NF mixed with graphene oxide to improve H$_2$ recovery with a supplied voltage of 0.8 V.[32] Due to the relatively low electrochemical activity of NF, graphene was used to increase the conductivity and provide a larger surface area through structure, reducing the overpotential and driving HER as a result.[33−35] Over three consecutive 8 h periods, NF with graphene was recorded with a higher maximum HPR (2.2 ± 0.3 m^3/m^3 day) than that of bare NF (which had maximum HPR ~ 1.7 m^3/m^3 day), demonstrating the effectiveness of graphene as an additional
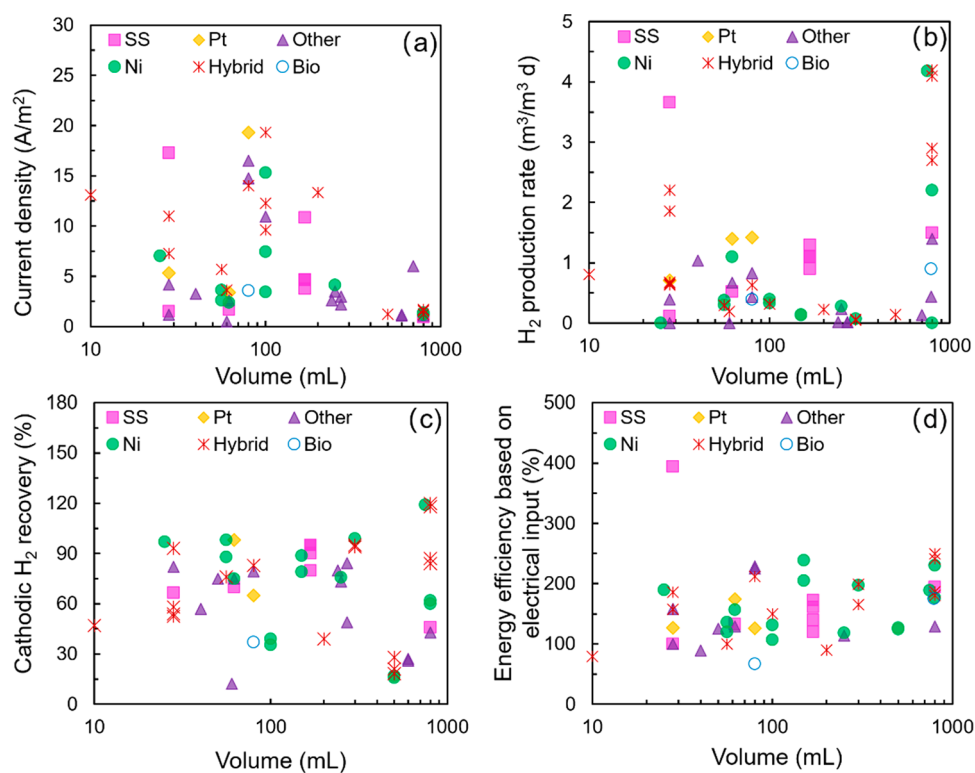
Figure 4. Different MEC performance measurements vs reactor volume. (a) Current density; (b) hydrogen production rate; (c) cathodic hydrogen recovery; (d) energy efficiency based on electrical input.

material for hybrid MEC cathode catalysts. Four types of SS materials (mesh, fiber felt, wool, and bush) were compared by running two-chamber MECs with 68 mL of volume and an external voltage of 0.9 V.[36] The four types of SS performed similarly and produced H_2 ranging from 0.9 to 1.3 m^3/m^3 day, with SS wool having the highest HPR due to its higher surface area. Overall, the materials with high HPR are mostly Ni-related and mostly mixed with other materials.

3.2. Energy Utilization

Figure 3c and d compares cathode materials by energy utilization efficiencies in MECs: energy efficiency based on electrical input (energy efficiency), η_E (%), and MEC overall energy efficiencies, η_{E+S}. Energy efficiency based on electrical input is defined as the ratio of the energy content of the H_2 produced to the applied electrical input:[3]

$$\eta_E = \frac{-W_{H_2}}{W_E} \tag{2}$$

where W_{H_2} is the energy recovered from H_2 produced and calculated based on heat of combustion or Gibbs free energy (<0) and W_E is the energy of the electrical input (>0). This is an important metric for MEC performance, as it shows the H_2 production performance relative to electrical input, which should optimally be increased for less energy consumption. In the past, Pt has been popular as the benchmark catalyst yielding a high performance in MECs. A study utilizing Pt/C as the cathode material reported a very high energy efficiency of up to ~450%,[19] though most studies reported efficiencies from 67.0% to 249.1%, with the exception of one outlier data point in the SS fiber felt category. This means the H_2 energy recovered can be higher than the electricity input. The Pt catalyst can be poisoned by phosphate ions, sulfur, and other

compositions, which leads to reduced efficiency.[37] The commercial 3D SS fiber felt, on the other hand, has a low cost[38] with good conductivity and higher surface area with relatively higher tolerance for salt poisoning.[18,39] Studies showed that SS fiber felt achieved a H_2 production rate of 3.7 ± 0.4 m^3/m^3 day with an energy efficiency of 394.4 ± 12.3%[19] but it experienced more corrosion over time.

Ni and Ni-based hybrid (Ni–Co, Ni–Co–P) catalysts have also become popular in recent years with most studies reporting an energy efficiency around 250%. Ni–Co, Ni–Co–P, and Ni catalysts with SS316 as the base cathode were recorded at 249.1%, 241.2%, and 230.3%, respectively.[31] The relatively high efficiency is partly due to a low electricity input (0.6 V) in the study, but it demonstrated the advantage of Ni-based cathodes that can be operated with low voltage input with low overpotential loss. The inclusion of electrodeposited Co in addition to electrodeposited Ni seems to yield slight improvement. A study using a carbon paper biocathode operated with 0.7 V reported a high energy efficiency of 225%, which is competitive with the Pt/C control cathode in the same experiment, suggesting a potential low-cost alternative in H_2 production from MECs.[40]

Figure 3d illustrates the distribution of MEC overall energy efficiencies, η_{E+S}, which is the H_2 energy produced from electrical energy and substrate:[3]

$$\eta_{E+S} = \frac{-W_{H_2}}{W_E - W_S} \tag{3}$$

where W_S represents amount of energy from the substrate which is also calculated by heat of combustion or Gibbs free energy (<0). It is worth noting that there are far less data points for overall efficiency compared to other metrics. As shown in Figure 3d, hybrid materials are the best performing
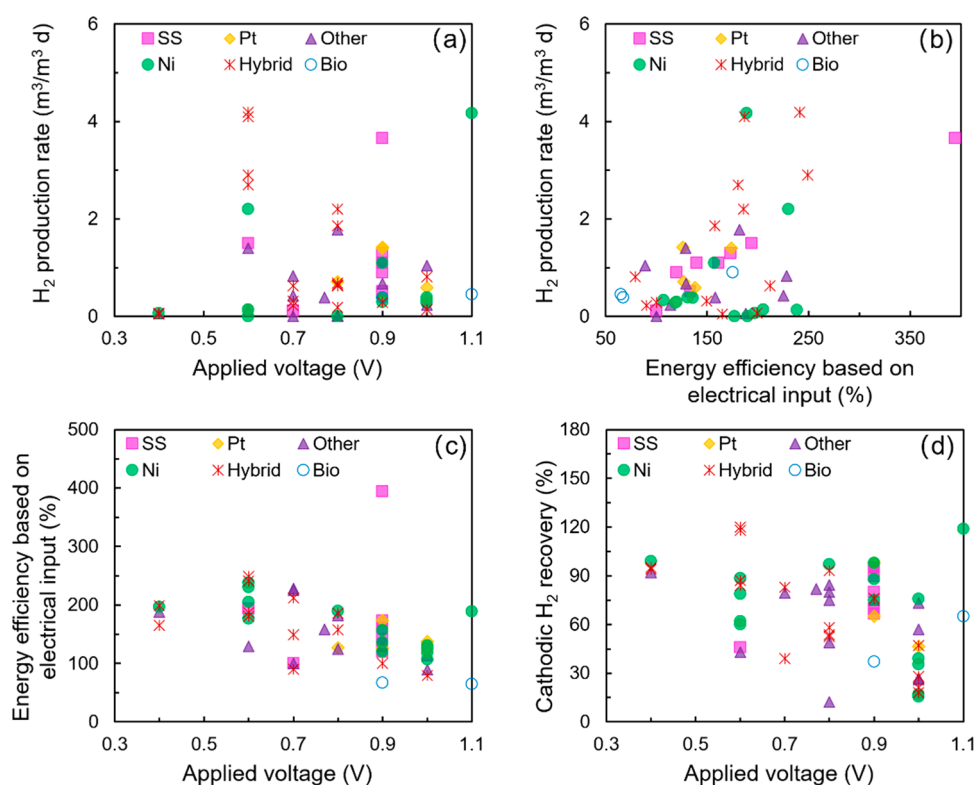
Figure 5. Performance measurement comparison for MEC cathode catalysts studied between 2012 and 2020. (a) Hydrogen production rate vs applied voltage; (b) hydrogen production rate vs energy efficiency based on electrical input; (c) energy efficiency based on electrical input vs applied voltage; (d) cathodic hydrogen recovery vs applied voltage.

category, followed by Ni materials. The best performing materials are the Ni−Co and Ni catalysts electrodeposited onto a SS316 base cathode at 98.4% and 92.4%, respectively.[31] The SS316 base cathodes outperformed the Cu base cathodes with the same catalysts and environment. The higher performance noted for SS316 might be due to the high concentration of Ni (8−14%) contained in SS316.[41,42] P supposedly increases conductivity and reduces system over-potential.[43] The inclusion of P lowered the overall efficiency of the SS316 cathode (82.1 ± 4%) but slightly increased the overall efficiency for the Cu cathode (75.2 ± 4%).

Looking at the general distribution of data points, a more consistent overall efficiency in MEC cathodes is necessary. The variation might be due to the difference in feed solution and bacteria performance, while low efficiencies occur when there is a failure to effectively utilize waste products.[44] Ni−P deposited on NF and operated in a single chamber MEC with 0.6 V of external voltage recorded an overall energy efficiency of 66.7%. The lower performance is likely due to using wastewater sludge, suggesting the existence of an issue and the need to bridge a gap between lab experiments and practical applications for MECs.

4. SYSTEM PERFORMANCE BASED ON REACTOR VOLUME

MEC applications are geared toward eventual large-scale operations, but a main challenge for system scale-up is the paradox between larger volume and higher performance. Previous experiments operated MEC reactors up to 1000 L in reactor volume,[45] which used a total of 144 SS304 cathodes and applied a constant voltage of 0.9 V. The HPR was around 0.1 m³/m³ day, and most H_2 was consumed by methano-

genesis. Several MEC pilots have been reported since then and have made good advancements. In a reactor of 10 L, Ni deposited on carbon paper as the MEC cathode catalyst was shown to produce H_2 at 1.0−2.6 m³/m³ day.[46] A 100 L MEC, using SS wool as the cathode and supplied with 1.1 V of external voltage, was able to achieve HPR of 0.6 m³/m³ day over a 12 month period using raw wastewater.[47] A similar pilot scale study using SS wool as the MEC cathode attempted a total volume of 130 L.[48] The HPR was 0.4 × 10⁻² m³/m³ day and the Coulombic efficiency (CE, percent of possible electrons transferred to the external circuit from the substrate removed) was 19%, indicating that the performance of the scaled-up MEC still needs improvements. Considering that we emphasize the development of novel MEC cathode materials in this Review and that the general scales of MECs with new cathode catalysts are small, we will only discuss performance relative to volume for novel MEC cathode catalysts research in this section without covering the details of pilot scale studies.

Figure 4 shows cathode performance measurements relative to the reactor volume. The metrics are current density, HPR, cathodic H_2 recovery, and energy efficiency based on electrical input for Figure 4a−d, respectively. Cathodic H_2 recovery is defined as the electrons recovered as H_2 vs theoretical electrons given by the current density:

$$r_{cat} = \frac{n_{H_2}}{n_{CE}} \tag{4}$$

where n_{H_2} represents the moles of H_2 actually recovered.[3]

In general, there seems no clear trends for current density, HPR, and cathodic H_2 recovery, because many factors influence the specific performance (e.g., materials, applied

voltage, substrate, configuration, etc.). Energy efficiency seems to be relatively unchanged when enlarging the MEC reactor because decreasing the applied voltage can help to alleviate energy loss in a larger MEC. As a rule of thumb, data points in the right upper corner indicate high performance in relation to relatively large volumes. We can see that, in Figure 4a and b, hybrid and Ni materials lie toward the right upper corner, which shows their potential for a larger volume of MEC.

It is worth noting that the highest HPR and cathodic H_2 recovery (4.2 ± 1 m^3/m^3 day and $119 \pm 5\%$, respectively) were achieved at a larger reactor volume of 750 mL by using an electroformed Ni mesh but the energy efficiency and CE were only $189 \pm 3\%$ and $75 \pm 4\%$, respectively.[17] The high HPR was likely caused by using a large external voltage supply (1.1 V), which consequently decreased the energy efficiency. Another large-scale study used Ni−Co−P, Ni, and No−Co as the catalysts in a two-chamber MEC with a volume of 800 mL.[31] This study only applied 0.6 V of external voltage, but it produced decent results across all tested cathodes. NF and Ni plates were also examined along with a SS mesh using sugar industry wastewaters.[49] A two-chamber MEC with a volume of 500 mL was used, and the external voltage supply was 1.0 V. Sugar cane industry wastewater (CSW) and raw sugar reprocessing industry wastewater (RSW) were compared; the study found that NF was the highest performing material, followed by the Ni plate and then SS mesh. For the MEC with the NF cathode and CSW substrate, the HPR was 1.6 mmol/L day, the cathodic H_2 recovery was 16.9%, the overall H_2 recovery was 10.0%, and the energy efficiency was 126.8%. Despite not reporting the highest performances, the study is valuable in that it provides data on how catalysts perform under real industrial wastewaters and shows that performance rankings of catalysts are consistent between CSW and RSW. Biocathodes have been studied with reactor volumes from 80 to 790 mL.[50−52] The highest biocathode HPR was 0.9 ± 0.1 m^3/m^3 day with a 790 mL reactor volume and 0.7 V of external voltage supply.

5. ENERGY INPUT

5.1. Influence of Applied Voltages in MEC Performance

Figure 5 examines two performances simultaneously to illustrate the relationship of cathode catalysts with energy inputs across multiple criteria. In principle, only 0.14 V of external voltage supply is required to make H_2 production favorable,[53] but in reality higher voltages (0.6−1.2 V) are applied to overcome overpotential losses. In general, higher applied voltages lead to improved H_2 production due to higher driving forces, but a balance between production rate and energy efficiency needs to be considered and implemented. Figure 5a illustrates how MECs with different cathode catalysts performed in terms of HPR and applied voltage from 2012 to 2020. Theoretically, an increase in applied voltage increases the HPR, but experimental evidence does not fully support this, suggesting increasing energy loss at higher applied energy.

Figure 5b draws a correlation between MEC performances combining HPR and energy efficiency based on electrical input. The slope of the data points indicates that HPR has a positive correlation with energy efficiency, indicating that higher electron utilization to produce H_2 can be achieved in a MEC with higher energy efficiencies. However, the data points with high energy efficiencies but low HPRs most likely represent the experiments with minimal electron losses given a

lower voltage. For those experiments conducted with a higher external voltage supply, energy losses increase due to the inability to effectively utilize all additional energy. These could be supported by the data shown in Figure 5c and d, which draws a connection between the energy efficiency based on electrical input and the applied voltage (Figure 5c) as well as the cathodic H_2 recoveries under various voltages (Figure 5d). The downward trends in these two figures clearly suggest the ability of MEC systems to optimally utilize electrons. Thus, there were some novel catalysts that exhibited good performance for H_2 production under high applied voltage, but their utilization of energy input was not satisfactory. For example, when 1.0 V was applied to conductive polymers of polyaniline mixed with multiwalled-carbon nanotubes, the HPR was 1.0 m^3/m^3 day but the CE was only 47% and the cathodic H_2 recovery was 56.7%.[54] Another experiment with a photo-assisted MEC with a polyaniline nanofiber cathode yielded a HPR of 1.8 m^3/m^3 day with an energy efficiency of 182% and overall energy efficiency of 66.2% at 0.8 V.[55] These results show that conductive polymers as MEC cathodes are suitable for H_2 production; however, their energy and recovery efficiencies can be further improved.

5.2. Overpotential in MECs

As shown in Figure 5c and d, higher applied voltage is not necessarily beneficial for energy efficiency and cathodic hydrogen recovery, which means higher electron loss happens under this condition. The reason for this electron loss is mainly due to overpotential. A high applied potential could produce a high current and thus promote ohmic losses as well as activation and concentration losses of electrodes.[24,56,57] These increased overpotentials would waste more electrons during the transformation of electrical and chemical energies into hydrogen energy in MECs, which exacerbates the contradicting challenge between H_2 production and voltage supply. Thus, one of the challenges for MECs is to reduce overpotential from an operation and design standpoint through reducing the activation, ohmic, and concentration overpotentials.[56] In this way, high levels of HPR can be achieved under lower applied voltage and allow for high energy efficiencies.

A challenge in MEC cathode catalyst studies is to find novel materials that surpasses precious metals, e.g., Pt, both economically and for reducing cathode potential loss.[58,59] Ni, especially NF, has become the leading catalyst when it comes to reducing overpotential.[20] An experiment in 2019 proved that Ni catalyst can achieve a HPR of 6.8×10^{-2} m^3/m^3 day under 0.4 V, which was competitive with the Pt control even if Pt had a higher surface area.[60] The study showed that metal nanoparticle catalysts (Ni, Cu, Pt) performed better than carbon-nanomaterial-based catalysts (carbon nanoparticles and carbon nanotubes) under 0.4 V as well. Another experiment tested two hybrid catalysts of nickel tungsten (NiW) and nickel molybdenum alloy (NiMo) deposits on a NF base at 0.6 V.[61] These two materials can enhance electrochemical properties to drive H_2 production through a synergistic electronic effect, thus reducing cathode overpotentials and yielding good HPRs of 0.14 ± 0.01 and 0.13 ± 0.01 m^3/m^3 day as well as and high energy efficiencies of $205.2 \pm 4.7\%$ and $238.4 \pm 11.3\%$, respectively. This shows the potential development of hybrid materials in being able to support electrochemical behaviors and cathode stability over an extended period.[62−64]

The highest cathodic H_2 recovery in Figure 5d is achieved using a NiFe layered double hydroxide catalyst with NF as the base cathode.[65] Using brewery wastewater as the substrate, this MEC reached a cathodic H_2 recovery of $99 \pm 0\%$, which is superior to those of Pt/NF ($84 \pm 3\%$), Pt/C ($83 \pm 0\%$), NF ($73 \pm 0\%$), and SS mesh ($76 \pm 1\%$). Most importantly, the HPR was 2.0 ± 0.0 m^3/m^3 day, which was on par with Pt/NF and Pt/C and roughly double that of NF and SS mesh. Another Ni related hybrid nickel powder blended with activated carbon was developed to reduce the amount of Ni and subsequent costs.[66] Although activated carbon, when used as cathode in a two-chamber MEC with 0.8 V of external voltage, only met a HPR of $3.0 \pm 0.4 \times 10^{-1}$ m^3/m^3 day and a cathodic hydrogen recovery of $12.3 \pm 0.1\%$,[67] it does provide great surface area, which is advantageous for high-performing HER catalysts.[68] Additionally, the technique of nitrogen doping improved the performance of activated carbon. The Ni powder loading of 4.8 mg Ni/cm^2 was found to be optimal for MEC H_2 production at 0.9 V, $3.8 \pm 0.4 \times 10^{-1}$ m^3/m^3 day, with a cathodic hydrogen recovery rate of 98.5%. When tested in a slightly larger MEC with a cathode area of 40 cm^2, not only did activated carbon with mg Ni/cm^2 have a HPR of 1.1 ± 0.1 m^3/m^3 day, which was marginally higher than that of NF, it also was cheaper to fabricate. Other materials, like SS fiber felt, brush, mesh, and wool, reported high cathodic hydrogen recoveries from 80 to 100%.[36] However, Figure 5c and d also exhibits excessive electron loss, a challenge that remains as the search continues for novel MEC cathode catalysts.

6. EMERGING CATHODE CATALYSTS IN THE PAST DECADE

Many new types of cathode catalysts were investigated for MECs in the past decade. For example, MoS_2 was first introduced as a MEC cathode catalyst in 2011[69] after its success in studies acting as a nitrogenase catalyst.[70] In the past few years, MoS_2 continued to capture research interest due to its HER activities being similar to those of Pt.[71] Despite its small free energy difference and good HER properties, MoS_2 lacks sufficient active sites and conductivity for a MEC cathode catalyst.[72] As a result, it is better utilized for forming hybrid catalysts with other materials, such as graphene oxide.[73] A MoS_2 nanocatalyst has been developed in conjunction with carbon cloth. When synthesized using the chemical exfoliation method, this hybrid catalyst was able to produce H_2 at a rate of 0.083 m^3/m^3 day with an applied voltage of 0.6 V, similar to that of the control Pt/CC cathode.[74] When treating wastewater, the MEC with a cathode of MoS_2 produced H_2 at a higher rate than that of SS (0.17 ± 0.03 vs 0.12 ± 0.02 m^3/m^3 day),[75] showing its potential in real-world applications. MoS_2 has been experimented in combination with nitrogen-doped graphene nanosheets, SS, and carbon nanotubes.[76−78]

Other than MoS_2, molybdenum sulfides (MoS_x) have been shown to support H_2 evolution in industrial wastewater.[79] In addition, titanium (Ti), a first-row transition metal like Ni, has also been considered as a possible alternative.[80,81] When tested as the bare cathode electrode, Ti mesh performed similar to Ni mesh and Pt/CC with 1.0 V of external voltage and a HPR of 0.23 ± 0.01 m^3/m^3 day. When used as a base electrode coated with Ni, Ni/Ti had a slightly higher HPR than that of Ni coated graphene (0.39 ± 0.01 vs 0.33 ± 0.03 m^3/m^3 day). Similarly, some metal oxides such as Ni and Co oxides are being developed based on transition metals.[82−84] Phosphorus and sulfide were added in hybrid catalysts to provide additional

electrochemical properties as well.[85−87] Although there are data points that were not thoroughly discussed, the data accurately reflects the progress made in recent MEC catalyst developments: iron-based composite nanorods with graphite carbon, Pt coated SSW, MoS_2 coated SSW, $Ni(OH)_2$ modified electrodes, Ni/Co on carbon paper, forms of individual Ni and SS materials, Ni_2P catalyst, NiO, MoO_2, and MoO_3 catalysts, polyaniline with graphene on SS, Ni and Co oxide nanocatalysts, and CoP-NF.[22,49,78,86,88−93]

7. PERSPECTIVES

MECs show good potential to concurrently achieve waste treatment and high rate renewable H_2 production. The pursuit of scale-up MEC applications continues to focus on the development of low-cost and high-performance cathode catalysts. In summary, this study covered approximately 70 MEC cathode catalysts from nearly 50 research experiments that specifically targeted novel MEC catalysts, the majority of which demonstrated enhanced H_2 production in various degrees. Interest in hybrid materials has emerged significantly. Hybrid materials are advantageous in that supplementary materials can achieve high structural and electrochemical performances as well as physical and chemical stability. On the other hand, several materials are commonly recognized as effective cathode catalysts, including Ni, SS, Cu, Co, MoS_2, graphene, etc. Specifically, NF and SS appear to have become the most common MEC cathode catalysts and base materials after Pt/CC. Some studies have even begun to use NF and SS as controls when testing new MEC cathode materials. Recently, nanotechnology has been used in multiple studies to provide structural advantages and stable electrochemical characteristics. The development of polyaniline structured materials and metal oxides shows potential for further advancement as well.

There has been no significant breakthrough in terms of pure H_2 production performance in the past decade, as HPR mostly ranged between 1 and 5 m^3/m^3 day despite the development of many new materials. However, numerous novel catalyst materials were shown to be competitive in terms of H_2 production rates and energy efficiencies. Furthermore, some of these materials are more affordable for scale-ups when cost is considered. Table 1 shows the commercial prices of several popular catalyst metals (sourced from Alibaba.com).

Table 1. Commercial Costs of Several Catalyst Materials

catalyst material	price (dollar/g)
Pt	150
Ni	0.3
SS	0.002
Cu	0.008
Mo	0.07
Mg	0.05

Although several promising catalysts have been identified, further studies are required to assess the performance of large-scale MEC systems under real-world conditions. While novel catalysts have been demonstrated to exhibit suitable performances, it can be difficult to directly compare these catalysts when data are collected from separate experiments under different conditions. Therefore, studies conducted with uniformly designed experiments are necessary to ensure that results are comparable. The overall performance of MECs will

also depend on the advancement in other components of the system. Ultimately, the selection of catalysts for MEC H_2 production is determined by the assessment of performance and cost.

The cathode material development for H_2 evolution would shed light on other cathodic conversion processes in microbial electrochemical systems as well. For example, the knowledge gained for direct and indirect inward electron transfer provided more evidence that H_2 can be an ideal mediator for microbial electrosynthesis via CO_2 reduction. Compared to traditionally focused direct electron transfer by electroactive bacteria, boosting H_2 production would accelerate the CO_2 reduction rate and product yield.

The progress as summarized is promising, but further work is warranted to optimize the materials, catalysts along with system design, stability, costs, and ease of operation under real-world conditions. Because of the unique feature of MECs in effectively treating wastewater and simultaneously producing H_2 gas, this technology may hold significant potential to resolving the global water, energy, and climate problems.

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