

## Recent Advancement of Nickel Based-Cathode for The Microbial Electrolysis Cell (MEC) and Its Future Prospect

Totok Eka Suharto<sup>1,\*</sup>, Ibdal Satar<sup>2</sup>, Wan Ramli Wan Daud<sup>3</sup>, Mahendra Rao Somalu<sup>4</sup> and Kim Byung Hong<sup>5,6</sup>

<sup>1</sup>Department of Chemical Engineering, Faculty of Industrial Technology, Universitas Ahmad Dahlan Yogyakarta, Indonesia

<sup>2</sup>Department of Food Technologi, Faculty of Industrial Technology, Universitas Ahmad Dahlan Yogyakarta, Indonesia

<sup>3</sup>Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

<sup>4</sup>Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

<sup>5</sup>Korean Institute of Science and Technology, 136-791, Republic of Korea

<sup>6</sup>State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, China

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### Abstract

The cost of a cathode and/or catalyst in a microbial electrolysis cell (MEC) is one of the main factors that must be considered before its application in a reactor. More than 45 % of total MEC cost is contributed by cathode material. Currently, platinum (Pt) has become the primary option as cathode or catalyst in MEC because it has superior catalytic properties for hydrogen evolution reaction. The high-price of Pt and its prone to being poisoned by the buffer in the electrolyte, calls for an alternative cathode or catalyst study. Some non-precious metals such as nickel (Ni), titanium (Ti), stainless steel (SS) and composites were explored to replace Pt. Among these materials, Ni is one of the best options because it has excellent catalytic properties, inexpensive, commercially available, less over-potential, and less toxic to living organisms. In most reports, Ni was applied in MEC to produce hydrogen from wastewater which showed comparable performance to Pt. This paper reviews the current status and future prospect of Ni performance as the cathode or catalyst in MEC for hydrogen production, based on the hydrogen cathodic recovery and production rate.

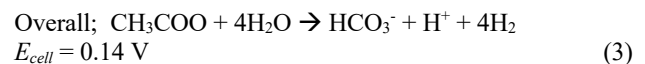
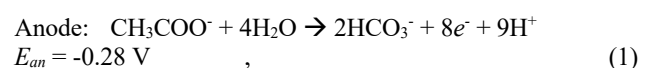
*Keywords:* Nickel, cathode, catalyst, MEC, hydrogen production

### 1. Introduction

Nowadays, the impact of conventional fuel usage on global warming has become the main problem facing humanity worldwide. Increase in carbon dioxide (CO<sub>2</sub>) level in the atmosphere has exceeded the limit, in which its concentration has reached 405 ppm [1-3]. This fact raises a negative impact on the living ecosystem like humans, microorganisms, or plants. It is a common perception that CO<sub>2</sub> pollution is mainly caused by transportation, industrial activities, electricity, and heat, including agriculture [4]. Various research approaches have been recommended to reduce the CO<sub>2</sub> level, such as the use of bio-hydrogen as an alternative fuel [5, 6] and converting CO<sub>2</sub> into value-added products via a biological electro-synthesis technology [7-10]. Either bio-hydrogen production or CO<sub>2</sub> reduction can be performed via a bio-electrochemical method. Microbial electrolysis cell (MEC) is for generating hydrogen [11] while microbial electro-synthesis systems (MES) is for reducing CO<sub>2</sub> [12].

Generally, MEC systems are divided into two compartments, namely anode, and cathode parts. In a dual-chamber system, the anode and cathode parts are separated by a membrane while in a single-chamber system, the membrane is removed. The hydrogen production happens in the cathode via proton reduction in the presence of electrons. The hydrogen production is a non-spontaneous reaction ( $E_{cell} = 0.14 \text{ V}$ ) [12] (Equation 1, Equation 2 and Equation 3), and thus an additional voltage ( $E_{ap}$ ) of ~ 0.14 V (theoretically) to

0.2 V or practically more must be supplied into the system. In addition, to accelerate the hydrogen evolution reaction (HER) at the cathode, the materials and/or catalysts play a significant role to overcome the thermodynamic barrier.



The cathode materials in the bio-electrochemical system (BES) have become the main issue and are believed to be the biggest contributor to the total cost of the system. The estimation of capital cost indicates that more than 45 % of total BES cost is contributed by cathode material (Figure 1) [13]. Research has introduced various approaches to eliminate the cathode and/or catalyst costs, such as the use of biological catalyst at the cathode surface [11, 14, 15] or the use of an alternative non-precious metal [16-20] and metal composites, such as nickel foam-graphene [21, 22].

So far, there are no papers that have comprehensively reviewed and summarized the feasibility of non-precious metal, particularly Ni, as the cathode and catalyst in MEC. Therefore, in this paper we discuss the potential of Ni as one of the non-precious metals that can be used as cathode and/or catalyst material. The selection of Ni was based on several

\*E-mail address: totok.suharto@che.uad.ac.id

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criteria, such as its catalytic activity comparable with Pt, high electrical conductivity, relatively inexpensive cost, commercial availability and low toxicity to microorganisms [16, 22].

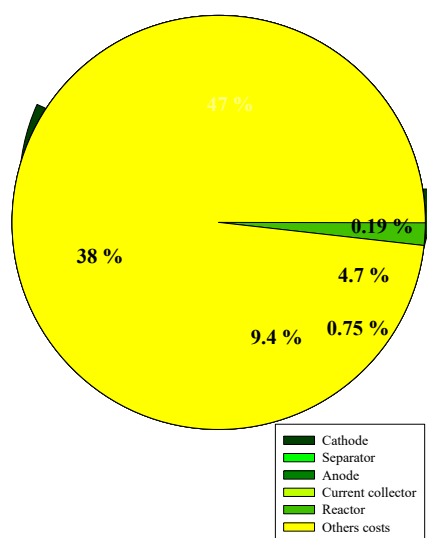


Fig. 1. Estimated capital cost of bio-electrochemical systems (BESs) in laboratory. (Source: [13])

## 2. Microbial Electrolysis Cells (MEC) Reactor Configurations

The MEC is one of BES types which is developed to produce hydrogen from organic materials. The MEC systems can be categorized into two configurations, namely single-chamber and dual-chamber MEC systems. It is well known that the performance and cost of the systems are associated with the construction. Since both single-chamber and dual-chamber have advantages and disadvantages, the selection of construction depends on the main study target.

### 2.1 Single Chamber MEC

To reduce cost to approximately 38% of total BES cost [13] and simplify the reactor construction [23], a single-chamber (membraneless) MEC system is recommended to produce hydrogen [24, 25] and/or methane [26, 27]. The typical single-chamber configuration is as shown in Figure 2. Since the absence of a separator can reduce ohmic cell resistance, the amount of biogas from a single-chamber MEC system is higher as compared to a dual-chamber MEC system (with membrane) [28]. The maximum hydrogen production rate using a single-chamber MEC system is around 180-fold higher than that obtained using a dual-chamber MEC system [11].

However, the system has a few disadvantages, such as low purity of hydrogen, the crossover of electrolyte and microorganisms, and possible short circuit occurrence in the reactor. Biogases, such as hydrogen, methane, and carbon dioxide were mixed in the same chamber. Based on literature, the biogas consists of hydrogen (80 % – 90 %), methane (1.9 % – 3.7 %), carbon dioxide (7 % – 8 %) and the remaining factor is nitrogen [30, 31]. Moreover, the hydrogen yield might be gradually reduced along with methane production in the presence of methanogens if the mixed-culture is used as an inoculum in the system [28]. Chemicals such as 2-

bromoethanesulfonate and lumazine are commonly injected into the reactor to inhibit methanogens activity [32] and keep the hydrogen production constantly high.

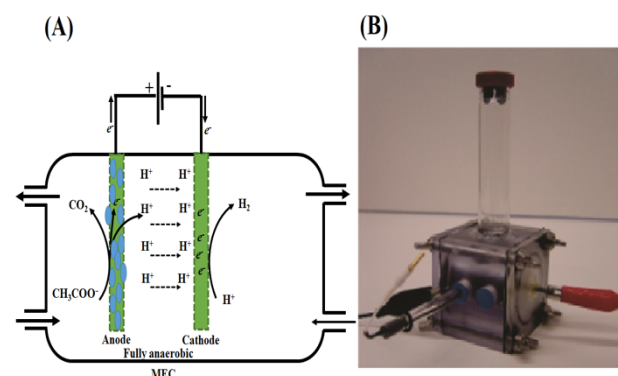


Fig. 2. Schematic (A) and photograph of single chamber (membraneless) MEC configurations (B). (Figure 2 (B) is reprinted from [29] Copyright © 2008, American Chemical Society)

### 2.2 Dual Chamber MEC

Figure 3 shows a typical dual-chamber MEC system reactor construction. In the system, a separator is placed between the anode and cathode, which is aimed to maintain hydrogen purity, eliminate microorganisms and fuels crossover, avoid any short circuits and prevent the methanogens consumption of the hydrogen gas [33]. Based on a report by [34], there was no trace of methane and carbon dioxide found in the cathode chamber. Therefore, the hydrogen purity was high. So far, the maximum hydrogen purity obtained was more than 95 % (the remaining factor was nitrogen gas) [35]. Besides, the dual-chamber MEC system construction was successful in generating hydrogen with extremely high  $Q_{H_2}$  of 50  $m^3/m^3/d$  [35].

The amount of hydrogen production is associated with some parameters, such as the type of organic substrates, inoculums, applied voltage, electrolyte pH, temperature, operational mode (batch or continuous), and reactor construction. The separator will also affect the amount of hydrogen production [36] because the presence of a separator will affect the microbial community dynamics, increase ohmic losses, and concentration overpotentials [37]. Currently Nafion 117 and the cation exchange membranes (CEM, CMI 7000) are generally used in laboratory scale application. In addition to the cost, the correct combination of all parameters is an essential requirement to generate a high amount of hydrogen.

## 3. General Components in MEC

In an MEC system, the electrode plays a key role in oxidation and reduction reactions. The oxidation reaction occurs at the anode, while the reduction reaction occurs at the cathode. The anode generates protons and electrons, and the cathode accelerates the hydrogen formation. Generally, the electrode materials must have adequate physical-mechanical strength, must not be prone to erosion by electrolyte, reactants, or product and must be resistant to cracking. The cathode materials must be chemically resistant to corrosion, unwanted oxide or hybrid formation, and deposition of inhibiting organic films under all conditions [38].

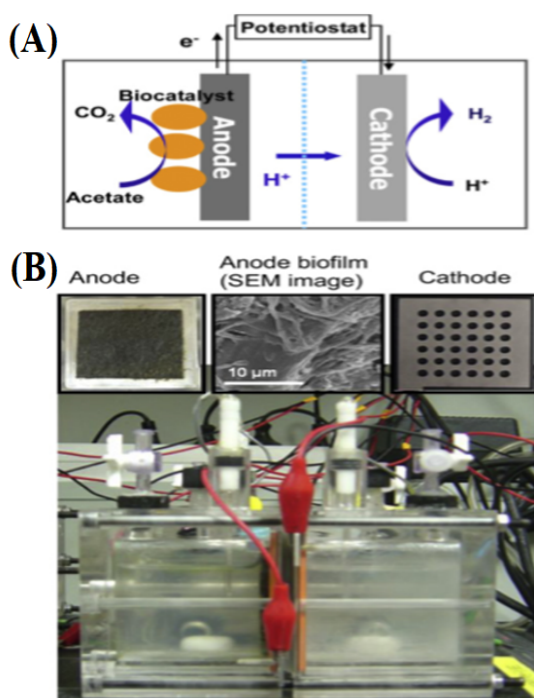


Fig. 3. Schematic (A) and photograph of dual-chamber MEC configuration (B) [32]. (The figure is reprinted with permission from Elsevier, license No. 4545750852997)

### 3.1 Electrodes: Anode and cathode

Most of the studies of MEC used carbon-based materials as the anode because it is friendly to microorganisms, inexpensive, conductive, commercially available, chemically stable in the long term, and non-corrosive. There is no crucial issue with anode material, whether its performance or impact on the environment. In terms of cost, less than 10 % of the total BES cost is contributed by anode materials. Whereas in terms of performance, microorganisms are easily attached on the surface to form a biofilm. The price of carbon-based material (i.e., graphite felt, GG) is relatively cheap, which is around \$ 65.00 for the size of 20 cm x 20 cm [38]. Although metal materials such as stainless steel (SS) is cheaper (\$ 18.00 for the size of 70 cm x 70 cm) than carbon-based anode and it can also be used as the anode, the microorganisms are practically difficult to attach on the SS surface. Several carbon-based materials are used as anode, namely carbon cloth (CC) [39, 40], carbon paper (CP) [41], carbon felt (CF) [32, 42], graphite brush (GB) [22, 29], graphite granules (GG) [26, 43], graphite plate (GP) [44], graphite rod (GR) [23], and graphite felt (GF) [6, 35, 45].

Similarly, the cathode can also be fabricated from carbon-based materials, composites, and metal alloy. Although carbon-based materials are suitable for the cathode, its catalytic properties for hydrogen evolution reaction is low. The cathode must have high catalytic activity to accelerate the hydrogen formation, and hence, a treatment or modification process is needed to improve the catalytic properties. Besides being used as cathode, several metal materials can be used as a catalyst, such as platinum (Pt), palladium (Pd), nickel (Ni), and titanium (Ti). These metals are coated or deposited onto the substrate surface by using spray, hydrothermal, or electrodeposition technique.

### 3.2 Separator

Ideally, the good inexpensive separator should have a minimum crossover of fuels, gases, microorganisms, and protons or other ions. The performance of separators is very

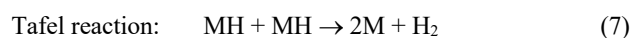
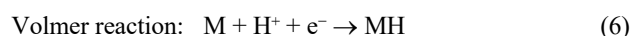
related to their material properties, thickness, and surface morphologies, as well as the operating conditions of the MEC system [46, 47]. Separators are generally categorized into two types, namely ion exchange membrane (IEM) and salt bridge. In the MEC applications, IEM such as Nafion and cation exchange membrane (CEM) are more popular. Several separators that are used include Nafion 115 [48], Nafion 117 [49] and CMI 7000 [50, 51]. The performance of a separator is associated with the duration time of MEC system operation, the biofilm formation and the ion accumulation are stopped on the separator surface [47].

## 4. Hydrogen evolution reaction (HER) metal cathode

The organic substrates are electrolyzed by electroactive bacteria (EAB) at the two electrodes to form hydrogen gas. At the anode, the substrate (acetate) is oxidized by EAB into protons, electrons, and bicarbonate, while at the cathode the protons are reduced to hydrogen gas, which is known as hydrogen evolution reaction (HER). The HER is a classical model of electrocatalysis process, which refers to the adsorption of hydrogen at the electrode surface [52-54]. The overall reaction of HER at low and high pH is described by Equation 4 and Equation 5, as follows:



The HER is a multistep reaction that can occur either in acid (low pH) or alkaline (high pH) conditions, as described by the Volmer-Tafel-Heyrovsky reactions. In the first step, protons in the electrolyte are initially reduced to hydrogen atom at the cathode surface (Equation 6). This step is known as Volmer reaction. In the next step, HER can occur according to two different reactions, which are either as a chemical reaction (Equation 7) or as an electrochemical reaction (Equation 8). The chemical process is then known as Tafel reaction while the electrochemical process is known as Heyrovsky reaction. The protons could be replaced with water molecules as the reactant if these reactions occurred in an alkaline condition.



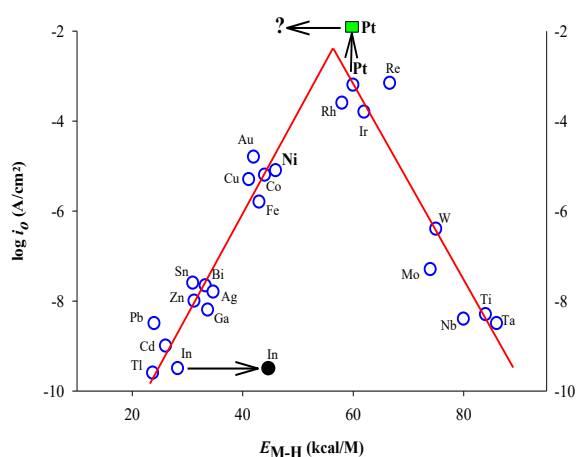
The HER is dependent on the structure of cathode surface, experimental condition, and cathode material. Therefore the HER mechanism is not only relevant for the basic understanding, but also real applications [53, 54].

### 4.1 The selection of Ni material

Since the complexity of metal behavior and poor detailed insight, the theory and empirical approaches must be used for the selection of cathode materials [55]. Initially, the selection of materials is based on experience and then tested in extensive research. Without extending the study under realistic condition, it is complicated to predict the performance and lifetime of the cathode [52]. Several material properties must be considered as guidelines, namely physicochemical properties, stability, rate, and product

selectivity, electrical conductivity, lifetime, cost, and environmental effect [56, 57].

The HER activation overpotential of materials varies considerably among metals [53]. For instance, Pb, Hg, and Cd need a high overpotential to accelerate the HER, and hence, they are not suitable as a cathode in MEC applications [57]. Meanwhile, Group 8, Group 9, and Group 10 in d-Block of the periodic table have low overpotentials [58]. The “volcano” curves (Figure 3) describe plots of catalytic metal activity versus the metal-hydrogen (H) bond strength [59]. The metal-H bond at the optimum curves is not too weak and not too strong, which means that the hydrogen can sufficiently cover the metal surface and at the same time, the adsorbed hydrogen on the surface is not immobilized [52, 59]. Based on Figure 4, the Pt, Rh, Re, and Ir metals are close to or at the top of the “volcano” curves, which means that they have high catalytic properties and low overpotential for HER. Unfortunately, these groups are more expensive materials as compared to Ni. For instance, the Pt price of \$ 838.00/oz was much higher as compared to the Ni price of \$ 93.76/oz [60].



**Fig. 4.** The “volcano” curve collected from [52] with corrected value. (Source: The figure is reprinted with permission from Elsevier, license No. 4551231372252)

Usually, a non-precious metal such as Ni is often employed for water electrolysis process [61-63]. However, Ni has high overpotential, and hence should be reduced to obtain excellent performance. There are a few conventional approaches that can be used to reduce the overpotential, namely by alloying the metal and increasing the surface area of metal [64]. These approaches are essential strategies for Ni to be selected before applied as the cathode in the MEC system.

#### 4.2 Nature of Ni Material

Nickel (Ni) was first isolated and classified as a chemical element by Swedish alchemist Baron Axel Fredrik Cronstedt [65]. In the industrial sector, Ni tends to play an important role that acts as a supportive and stabilizing material. Ni can be combined with other metals to produce a stronger product, which is shinier and more durable and as a protective outer coating to protect the surface of softer metals. Besides, Ni can also be used as a catalyst for the hydrogenation of unsaturated compounds in several types of oils and converting substances from liquids to solids. Ni is the fifth most abundant element in the universe. It is a transition metal, which means that it has valence electrons in two shells of one, so Ni allows the formation of several different oxidation states [66]. Physicochemical properties of Ni are hard, robust and silver-

white color, ductile, and resistant to heat and corrosion. Therefore, Ni is beneficial for the development of a wide variety of materials, such as wires, plates, coins, and other military equipment [65, 67]. Pure Ni is in powder form, and hence the small pieces (high surface area) show high reactivity and significant chemical property. However, in larger pieces (low surface area), Ni is slow to react with air under standard condition because of the presence of an oxide layer that inhibits further corrosion [68].

Table 1 shows the selected physical characteristics of metals. The appropriate combination between physical and chemical properties is essential for successful fabrication and application of the cathode into the reactors. Usually, the cathodes are from a combination of some pure metals, known as alloy, because the physicochemical properties of alloy are better than pure metals [56]. Electrical conductivity is the critical property in the selection of cathode material since it determines the magnitude of voltage drop, and is associated with electrode overpotential and catalytic activity.

**Table 1.** Selected physical characteristics of pure metals [69]. Considered mainly as pure metal [56].

Electrodes	Density (g/cm <sup>3</sup> )	R (10 <sup>-6</sup> Ω cm)	E° (Volts) vs. SHE
Au <sup>3+</sup> + 3e <sup>-</sup> → Au	18.88	2.04	+ 1.50
Pt <sup>2+</sup> + 2e <sup>-</sup> → Pt	21.45	9.80	+ 1.19
Pd <sup>2+</sup> + 2e <sup>-</sup> → Pd	12.00	10.5	+ 0.92
Cu <sup>2+</sup> + 2e <sup>-</sup> → Cu	8.92	1.56	+ 0.34
WO <sub>3</sub> + 6H <sup>+</sup> + 6e <sup>-</sup> → W <sub>(s)</sub> + 3H <sub>2</sub> O	19.30	11.2	- 0.09
Pb <sup>2+</sup> + 2e <sup>-</sup> → Pb	11.34	19.00	- 0.13
Sn <sup>2+</sup> + 2e <sup>-</sup> → Sn	7.28	1.50	- 0.13
Ni <sup>2+</sup> + 2e <sup>-</sup> → Ni	8.90	6.10	- 0.25
Fe <sup>2+</sup> + 2e <sup>-</sup> → Fe	7.86	8.90	- 0.44
Zn <sup>2+</sup> + 2e <sup>-</sup> → Zn	7.13	6.0	- 0.76
MoO <sub>2(s)</sub> + 2H <sub>2</sub> O + e <sup>-</sup> → Mo <sub>(s)</sub> + 4OH <sup>-</sup>	10.20	5.38	- 0.98
Mn <sup>2+</sup> + 2e <sup>-</sup> → Mn	7.30	1.44	- 1.18
Ti <sup>3+</sup> + 3e <sup>-</sup> → Ti	4.50	43.10	- 1.37

#### 5. Performance of Ni material in MEC

The good performance of electrode material is a mandatory requirement in the MEC system before its application in the real condition. Here, the performance of Ni, either as cathode or catalyst, will be discussed based on the hydrogen cathodic recovery (*r*H<sub>2-Cat</sub>) and production rates (Q<sub>H<sub>2</sub></sub>) and compared to Pt performance. The collection of literature was from journals within years ranged from 2008 to 2018.

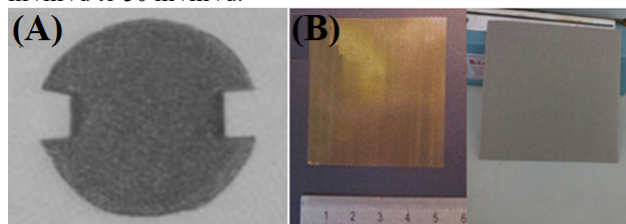
##### 5.1 Ni as cathode

Based on the Ni composition, the type of Ni material is divided into two categories, namely single or pure Ni material and its alloys. The materials, which consist of Ni ≥ 99% are categorized as single Ni while the materials which consist of various metals, such as iron (Fe), Molybdenum (Mo), and Chromium (Cr), with Ni as a significant element, are categorized as Ni alloy (Table 2). Several single Ni materials are used as the cathode in MEC system, such as Ni 110, Ni 210, and Ni 255 [16], Ni foam (NF) [18, 35] and Ni mesh (NM) [44]. Meanwhile, Ni alloys, such as Ni 400, Ni 625, and NiHX performances have also been reported by [16].

**Table 2.** Typical element compositions for single Ni and alloys; (Source: Data collected from [16, 25])

Materials	Element compositions (%)						
	Ni	Fe	Mn	Mo	Cr	Cu	Others
Ni 110	>99						
Ni 210	>99						
Ni 255	>99						
NiO <sub>x</sub> 87302	>99						
Ni 201	99	0.4	0.35			0.25	
Ni 400	65.1	1.6	1.1			32	
Ni 625	61	2.5		9	21.5		6
Ni HX	47	18		9	22		4

Element compositions, shape, and morphology play a crucial role in the catalytic activity of materials [70]. The presence of other elements, such as iron (Fe) in Ni alloy, can improve the performance. For example, Ni 625 (with Ni 61%, Fe 2.5 %, others 36 %) produce  $Q_{H_2}$  of  $0.79 \pm 0.27 \text{ m}^3/\text{m}^3/\text{d}$ , which is much higher than  $0.38 \pm 0.04$  by using Ni 201 (Ni 99 %, Fe 0.4 %, others 0.6 %) [16]. The high Fe composition results in high Ni alloy performance. However, there is no report on the optimum composition of Fe in Ni alloys. In terms of shape and morphology, the high surface area and porosity, such as NF and NM, show better performance as compared to Ni plates like Ni 201, Ni 400 and Ni HX. Figure 5 shows the typical Ni materials, in which both NF and NM have a high surface area. Both NF and NM produced  $Q_{H_2}$  of  $50 \text{ m}^3/\text{m}^3/\text{d}$  ( $E_{ap} = 0.9 \text{ V}$ ) [35] and  $4.18 \pm 1.00 \text{ m}^3/\text{m}^3/\text{d}$  ( $E_{ap} = 1.1 \text{ V}$ ) [44], which were much higher than the Pt sheet ( $Q_{H_2} = 0.68 \pm 0.06$  at  $E_{ap} = 0.9 \text{ V}$ ) [16]. In overall the Ni performance is as shown in Table 3. In the 2010 to 2016 period, the data reported that Ni as cathode produced  $Q_{H_2}$  in the range of  $0.38 \text{ m}^3/\text{m}^3/\text{d}$  to  $50 \text{ m}^3/\text{m}^3/\text{d}$ .



**Fig. 5.** Typical Ni metal materials; (A) nickel foam (NF) [71] and (B) nickel mesh (NM) [44]. (Source: Figure 5(A) and Figure 5(B) are reprinted with permission from Elsevier, license No. 4552400174955 and 4552391082754.)

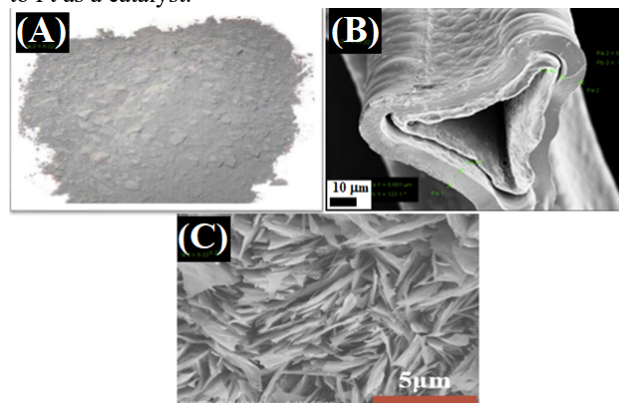
## 5.2 Ni as catalyst

The cost of Ni plate, foam, mesh, or powder is still high. Additionally, the corrosion of the cathode can inhibit the intrinsic catalytic activity over time that cannot be restored without replacement [25, 72, 73]. For instance, Ni-based cathodes show a high hydrogen production rate at the early stage of MEC system operation, but the performance is gradually declined over time [35]. Ni particles application can reduce cost as well as the amount of metal used, compared to Ni plates, foam, mesh, or powder.

There are several methods which are generally used to deposit Ni particles on the substrate, such as electrodeposition [30, 39, 74, 75], hydrothermal [61, 76], and spray [77].

Among these methods, electrodeposition is more favorable than others due to its easy operation, relatively low cost and simple method. Ni particles can be coated on the substrate surface through electrodeposition or plating. A combination of Ni with other metal particles, such as molybdenum (denoted as NiMo), tungsten (NiW) [64, 78], cobalt (NiCo) [64], iron and layered double hydroxide (NiFe-LDH) [76] have been investigated. Moreover, single Ni particles can also be coated on the substrate of SS A286 (SS A286-eNiO<sub>x</sub>) [16], titanium (Ti/Ni) [75, 79], graphite felt (GF/Ni) [75]. Ni 625 (Ni 625 + eNiO<sub>x</sub>), Ni foam (NF-Ni) [80], nickel-phosphorus (Ni-P). Among these catalysts, Ni-P and NiMo show the good performance by producing  $Q_{H_2} = 2.29 \pm 0.11 \text{ m}^3/\text{m}^3/\text{d}$  and  $Q_{H_2} = 2.1 \text{ m}^3/\text{m}^3/\text{d}$ .

Figure 6 shows the typical example for Ni powder (A) and the micrograph images of Ni catalyst coated on the substrate (B, C) applied in MEC. Ni powder is mixed with a carbon-based catalyst such as carbon black (CB-Ni) [25], and activated carbon (AC-Ni)[73] are coated on the substrate surface through the spray method. Like Pt catalyst, Ni powder can also be coated on the substrate surface (i.e., graphite felt) by using a binder, such as a polytetrafluoroethylene (PTFE) or Nafion solution. As discussed above, the selection of Ni material should refer to several criteria, such as surface area, particle size, and porosity. Principally, the high specific surface area, porosity, and smaller particle size have high catalytic activity and current density [70, 79]. For example, Ni 210 powder (surface area of  $0.60 \text{ m}^2$  and a particle size of  $0.5 - 1.0 \mu\text{m}$ ) shows an overpotential of  $-0.500 \text{ V}$ , which is lower than  $-0.720 \text{ V}$  for Ni 110 (surface area of  $0.17 \text{ m}^2$  and particle size of  $1 - 2 \mu\text{m}$ ) and  $-0.760 \text{ V}$  for Ni 10225 (surface area of  $0.24 \text{ m}^2$  and particle size of  $2.2 - 3 \mu\text{m}$ ) [25]. Lower overpotential will result in higher catalytic activity for HER [81]. Therefore, the Ni 210 material is chosen rather than Ni 110 and Ni10225 as cathode catalyst in MEC application [25]. So far, Ni powder as a catalyst is successful in producing  $Q_{H_2}$  in the range of  $0.27 \text{ m}^3/\text{m}^3/\text{d}$  to  $2.1 \text{ m}^3/\text{m}^3/\text{d}$ . Overall, these data mean that the performance Ni as a catalyst is comparable to Pt as a catalyst.



**Fig. 6.** The typical Ni powder (A) and Ni catalyst coated on the surface of substrate (B, C) used as cathode catalyst in MEC application. Figure 6(A) collected from [38], and Figure 6 (B, C) reprinted with permission from Elsevier, license No. 4615240856504

**Table 3.** Summary of selected performance of nickel as cathode and catalyst in MEC applications in the 2008 to 2018 period.

Material	Type of MEC	$E_{ap}$ (V)	Substrate	$r_{H_2-Cat}$ (%)	$Q_{H_2}$ ( $\text{m}^3/\text{m}^3/\text{d}$ )	Ref.
Ni as Cathode						
Ni 210 powder	Single Chamber	0.6	Acetate	$79 \pm 10$	$1.3 \pm 0.3$	[25]
Ni 210 powder	Single Chamber	0.8	Acetate	NA	1.85	[25]
Ni foam	Single Chamber	0.9	Acetate	$34.5 \pm 0.8 \text{ mL}^*$	1.1	[71]
Ni foam	Single Chamber	0.8	BWW	$73 \pm 0$	$1.13 \pm 0.01$	[76]

Ni foam	Single Chamber	0.8	FE	69 ± 0	1.07 ± 0.01	[76]
Ni foam	Dual Chamber	1.0	Acetate	90	50.0	[35]
Ni Mesh	Single Chamber	1.1	Acetate	119 ± 5	4.18 ± 1	[44]
Ni 201	Single Chamber	0.9	Acetate	27 ± 4	0.38 ± 0.04	[16]
Ni 400	Single Chamber	0.9	Acetate	31 ± 5	0.41 ± 0.10	[16]
Ni HX	Single Chamber	0.9	Acetate	40 ± 8	0.55 ± 0.11	[16]
Ni 625	Single Chamber	0.9	Acetate	43 ± 9	0.79 ± 0.27	[16]
NF-Graphene	Dual Chamber	0.8	Acetate	NA	1.31 ± 0.07	[22]
Pt powder	Single Chamber	0.6	Acetate	89 ± 7	1.6 ± 0.0	[25]
Pt sheet	Single Chamber	0.9	Acetate	47 ± 2	0.68 ± 0.06	[16]
Stainless steel mesh	Single Chamber	0.6	Acetate	83 ± 8	1.7 ± 0.1	[72]
<i>Ni as Catalyst</i>						
Ni 210-CB	Single Chamber	0.6	Acetate	94 ± 5	1.2 ± 0.1	[25]
Ni-P	Single Chamber	0.9	Acetate	86.8 ± 3.4	2.29 ± 0.11	[82]
eNiOx	Single Chamber	0.6	Acetate	86 ± 1	0.9 ± 0.1	[25]
NiFe-LDH/ Ni foam	Single Chamber	0.8	BBW	99 ± 0	2.01 ± 0.01	[76]
Ni-AC/SS	Dual Chamber	0.9	Acetate	88 ± 2	1.1 ± 0.1	[73]
NiCo	Single Chamber	0.7	Acetate	NA	0.57*	[30]
NiMo	Single Chamber	0.6	Acetate	90	2.1	[39]
Bio-cathode	Single Chamber	0.6	Wastewater	54.3	0.72	[83]
Pt/CNT	Single Chamber	0.6	Acetate	89 ± 7	1.6 ± 0.0	[25]
Pt/CC	Single Chamber	1.1	Acetate	121 ± 3	4.25 ± 1.8	[44]

## 6. Future Studies on Ni material in the MEC application

The Ni materials as cathode or catalysts in MEC applications is a new approach that could play a critical role in leading recent attempts towards the delivery bioelectrochemical technology (BET) out of lab-scale into the real implementation by replacing the noble metal cathode. In addition to the low cost, commercial availability and environmentally friendly nature, the Ni material shows excellent performance for hydrogen production. Ni foam (NF) shows better performance compared to the Pt [35]. Also, Ni can be combined with other metals such as tungsten (W), cobalt (Co) and molybdenum (Mo) [64] to form alloys in order to increase the intrinsic catalytic activity for HER. Furthermore, the catalytic activity of stainless steel (SS) can be enhanced by deposited of Ni materials on their surface [16]. Hence, the extended studies are necessary to investigate the useful parameters, whether individually or integrally, and to improve the yields and durability of the systems [82]. Comprehensive studies are required to focus on the stability of Ni performance concerning the hydrogen production rate for long term MEC operation. The additional energy continuously supplied into the system can reduce the stability of Ni material; consequently, Ni can quickly react with other ions in the electrolyte. However, this is an assumption which needs to be revealed in further studies.

## 6. Conclusion

Scientifically, the feasibility of MEC for hydrogen production has successfully demonstrated by many kinds of research. However, commercialization is still far for MEC due to various constraints. One of them is an issue associated with the cost of the cathode and/or catalyst material for accelerating the hydrogen gas formation. In early MEC studies, Pt was typical as the cathode. The Pt is a precious metal, expensive and can potentially be poisoned in the presence of buffer, sulfur, nitric oxide, silicone, carbon monoxide, and hexamethyldisiloxane (HMDS) in the electrolyte. Indeed, Pt was assumed as the most efficient catalyst in many MEC applications for hydrogen evolution

reaction [16, 84], but it is not economical for real-world application.

Several materials are tested as a cathode or catalyst to show that Ni material is an excellent alternative to replace Pt. The single Ni or alloys are used in many MEC studies, either as a cathode or catalyst. As reported by Salemba et al. [16], the intrinsic catalytic activity of pure Ni metal is lower as compared to its alloy. So far, Ni alloy such as NF shows the best performance in which the hydrogen production rate is 50 m<sup>3</sup>/m<sup>3</sup>/d [35]. NF performance is 12-fold better as compared to Pt/CC catalyst (4.25 ± 1.8 m<sup>3</sup>/m<sup>3</sup>/d) [44]. This fact reveals that the feasibility of Ni is very interesting to be applied in the real MEC application. However, the performance of NF material is not consistent (even drop) along with MEC operations [25]. The presence of other elements in Ni alloy plays a significant role in the catalytic activity and physicochemical stability, and hence extended studies should be performed to provide the cathode materials successfully and with good quality in the future.

Additionally, the cathode performance is much related to the type of catalyst at the cathode. The correct combination of catalyst-cathode can produce cathode with excellent properties. So far, Ni-based catalysts such as Ni-P, Ni-LDH with NF (as substrate) and NiCo with CC produced Q<sub>H<sub>2</sub></sub> of 2.29 ± 0.11 m<sup>3</sup>/m<sup>3</sup>/d, Q<sub>H<sub>2</sub></sub> of 2.01 ± 0.01 m<sup>3</sup>/m<sup>3</sup>/d and Q<sub>H<sub>2</sub></sub> of 2.1 m<sup>3</sup>/m<sup>3</sup>/d which were higher than Q<sub>H<sub>2</sub></sub> of 1.6 ± 0.0 m<sup>3</sup>/m<sup>3</sup>/d for Pt/CNT catalyst. To find the precise composition of each element, the method, supporting materials and substrates should be intensively studied. Hence, with a few modifications, treatments and correct strategies in the cathode and/or catalyst preparation, the feasibility of Ni material in the MEC applications could fully replace Pt and become the primary option in the future.

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## References

1. R. Lal, *Energy Environ Sci*, 1 (2008) 86-100.
2. M.I. Hoffert, K. Caldeira, G. Benford, D.R. Criswell, C. Green, H. Herzog, A.K. Jain, H.S. Khesghi, K.S. Lackner, J.S. S. Lewis, H.D. Lightfoot, W. Manheimer, J.C. Mankins, M.E. Mauel, L.J. Perkins, M.E. Schlesinger, T. Volk, T.M.L. Wigley, *Science*, 298 (2002) 981-987.
3. R. Lindsey, <https://www.climate.gov/news-features/understanding-climate/climate-change-atmospheric-carbon-dioxide2018>.
4. <https://www.epa.gov/ghgemissions/sources-greenhouse-gas-emissions#commercial-and-residential>, 2016.
5. I.K. Kapdan, F. Kargi, *Enzyme Microb Technol*, 38 (2006) 569-582.
6. Y. Feng, Y. Cheng, Y. Du, Q. Teng, H. Li, *Int J Electrochem Sci*, 9 (2014) 6993-7002.
7. K.P. Nevin, T.L. Woodard, A.E. Franks, Z.M. Summers, D.R. Lovley, *ASM*, 1 (2010) 1-4.
8. S. Cheng, D. Xing, D.F. Call, B.E. Logan, *Environ Sci Technol*, 43 (2009) 3953-3958.
9. X. Christodoulou, T. Okoroafor, S. Parry, S.B. Velasquez-Orta, *J CO2 UTIL*, 18 (2017) 390-399.
10. A. El Mekawy, H.M. Hegab, G. Mohanakrishna, A.F. Elbaz, M. Bulut, D. Pant, *Bioresour Technol*, 215 (2016) 357-370.
11. R.A. Rozendal, H.V.M. Hamelers, G.J.W. Euverink, S.J. Metz, C.J.N. Buisman, *Int J Hydrogen Energy*, 31 (2006) 1632-1642.
12. K. Rabaey, R. Rozendal, A. Appl Ind Microb 8(2010) 706-716.
13. R.A. Rozendal, H.V. Hamelers, K. Rabaey, J. Keller, C.J. Buisman, *Trends Biotechnol*, 26 (2008) 450-459.
14. R.A. Rozendal, H.V.M. Hamelers, G.J.W. Euverink, S.J. Metz, C.J.N. Buisman, *Environ Sci Technol*, 42 (2007) 629-634.
15. V. Ruiz, Z.E. Ilhan, D.-W. Kang, R. Krajmalnik-Brown, G. Buitron, *J Biotechnol*, 182 (2014) 11-18.
16. P.A. Salembro, M.D. Merrill, B.E. Logan, *J Power Sources*, 190 (2009) 271-278.
17. P.A. Salembro, M.D. Merrill, B.E. Logan, *Int J Hydrogen Energy*, 35 (2010) 428-437.
18. W. Wang, L. Huang, H. Yu, X. Quan, Y. Li, G. Fan, L. Li, *Int J Hydrogen Energy*, 40 (2015) 184-196.
19. Y. Zhang, L. Yu, D. Wu, L. Huang, P. Zhou, X. Quan, G. Chen, *J Power Sources*, 273 (2015) 1103-1113.
20. Y.H. Ahmad, A.M.A. Mohamed, T.D. Golden, N. D'Souza, *Int J Electrochem Sci*, 9 (2014) 6438-6450.
21. M.G. Dashti, P. Abdesahian, W.M.W. Yusoff, M.S. Kalil, A.A. Hamid, *Hindawi*, 2014 (2014) 1-12.
22. W. Cai, W. Liu, J. Han, A. Wang, *Biosens Bioelec*, 80 (2016) 118-122.
23. C.G.S. Giddings, K.P. Nevin, T. Woodward, D.R. Lovley, C.S. Butler, *Front Microbiol*, 6 (2015) 1-6.
24. D.F. Call, R.C. Wagner, B.E. Logan, *Appl Environ Microbiol*, 75 (2009) 7579-7587.
25. P.A. Salembro, M.D. Merrill, B.E. Logan, *Int J Hydrogen Energy*, 35 (2010) 428-437.
26. P. Clauwaert, W. Verstraete, *Appl Microbiol Biotechnol*, 82 (2009) 829-836.
27. C.A.A. Mieke, V. Eerten-Jansen, A.T. Heijne, C.J.N. Buisman, H.V.M. Hamelers, *Int J Energy Res*, 36 (2012) 809-819.
28. B.E. Logan, D. Call, S. Cheng, H.V.M. Hamelers, T.H.J.A. Sleutels, A.W. Jeremiasse, R.A. Rozendal, *Environ Sci Technol*, 42 (2008) 8630-8640.
29. D.F. Call, B.E. Logan, *Environ Sci Technol*, 42 (2008) 3401-3406.
30. Y. Wang, Y. Zhao, A. Wu, Z. Dong, J. Li, J. Wang, *Int J Electrochem Sci*, 13 (2018) 10848-10858.
31. Y. Zhao, Z. Dong, Y. Wang, D. Yang, X. An, *Int J Electrochem Sci*, 14 (2019) 2883-2892.
32. K.-J. Chae, M.-J. Choi, K.-Y. Kim, F.F. Ajayi, I.-S. Chang, I.S. Kim, *Int J Hydrogen Energy*, 35 (2010) 13379-13386.
33. A. Kadier, Y. Simayi, P. Abdesahian, N.F. Azman, K. Chandrasekhar, M.S. Kalil, *AEJ*, 55 (2016) 427-443.
34. I. Rivera, G. Buitron, P. Bakonyi, N. Nemestothy, K. Be'laf-Bako, *J Appl Electrochem*, 45 (2015) 1223-1229.
35. A.W. Jeremiasse, H.V.M. Hamelers, M. Saakes, C.J.N. Buisman, *Int J Hydrogen Energy*, 35 (2010) 12716-12723.
36. S. Babanova, K. Carpenter, S. Phadke, S. Suzuki, S. Ishii, T. Phan, E. Grossi-Soyster, M. Flynn, J. Hogan, O. Bretschgera, *J Electrochem Soc*, 164 (2017) 3015-3023.
37. D. Ki, S.C. Papat, C.I. Torres, *CHEM ENG J*, 287 (2016) 181-188.
38. Fuel-Cell-Store, <http://www.fuelcellstore.com/02-ptc-cloth-electrode?search=carbon%20cloth>. Date accessed 16-03-2019.
39. H. Hu, Y. Fan, H. Liu, *Int J Hydrogen Energy*, 35 (2010) 3227-3233.
40. S. Chen, B.E. Logan, *Bioresour Technol*, 102 (2011) 3571-3574.
41. M. Villano, L. DeBonis, S. Rossetti, F. Aulenta, M. Majone, *Bioresour Technol*, 102 (2011) 3193-3199.
42. S. Hrapovic, M.F. Manuel, J.H.T. Luong, S.R. Guiot, B. Tartakovsky, *Int J Hydrogen Energy*, 35 (2010) 7313-7320.
43. K. Guo, X. Tang, Z. Du, H. Li, *Biochem Eng J*, 52 (2010) 48-52.
44. A. Kadier, Y. Simayi, K. Chandrasekhar, M. Ismail, M.S. Kalil, *Int J Hydrogen Energy*, 40 (2015) 14095-14103.
45. T. Jafary, W.R.W. Daud, M. Ghasemi, M.H.A. Bakar, M. Sedighi, B.H. Kim, A.A. Carmona-Martinez, J.M. Jahim, M. Ismail, *Int J Hydrogen Energy*, xxx (2018) 1-8.
46. S.M. Daud, B.H. Kim, M. Ghasemi, W.R.W. Daud, *Bioresour Technol*, 195 (2015) 170-179.
47. F. Harnisch, U. Schröder, *Chem Sus Chem*, 2 (2009) 921-926.
48. N. Aryal, A. Halder, M. Zhang, P.R. Whelan, P.L. Tremblay, Q. Chi, T. Zhang, *Sci Rep*, 7 (2017) 1-8.
49. C.W. Marshall, D.E. Ross, E.B. Fichot, S. Norman, H.D. May, *Appl Environ Microbiol*, 78 (2012) 8412-8420.
50. E.V. LaBelle, H.D. May, *Front Microbiol*, 8 (2017) 756.
51. R. Ganigue, S. Puig, P. Batlle-Vilanova, M.D. Balaguer, J. Colprim, *Chem Commun*, 51 (2015) 3235-3238.
52. O.A. Petrii, G.A. Tsirlina, *Electrochimica Acta*, 39 (1993) 1739-1747.
53. K.J. Vetter, *Electrochemical kinetics: theoretical and experimental aspects*, Academic press, New York, 1967.
54. A. Eftekhari, *Int J Hydrogen Energy*, 42 (2017) 11053-11077.
55. A.R. Zeradjanin, I.-P. Grote, G. Polymeros, K.J.J. Mayrhofer, *Electroanalysis*, 28 (2016) 1-8.
56. A.M. Couper, D. Pletcher, F.C. Walsh, *Chem Rev*, 90 (1990) 837-865.
57. A.W. Jeremiasse, The Netherlands Research School for the Socio-Economic and Natural Sciences of the Environment (SENSE), Wageningen University, Wageningen, NL, 2011, pp. 168.
58. M.H. Miles, *Electroanal Chem Interfacial Electrochem*, 60 (1975) 89-96.
59. L.A. Kibler, *ChemPhysChem*, 7 (2006) 985-991.
60. <https://www.dailymetalprice.com/>, 2019.
61. C. Hu, Q. Ma, S.-F. Hung, Z.-N. Chen, D. Ou, B. Ren, H.M. Chen, G. Fu, N. Zheng, *Chem*, 3 (2017).
62. M.J. Giz, S.C. Bento, E.R. Gonzales, *Int J Hydrogen Energy*, 25 (2000) 621-626.
63. P.-C. Chen, Y.-M. Chang, P.-W. Wu, Y.-F. Chiu, *Int J Hydrogen Energy*, 34 (2009) 6596-6602.
64. C. González-Buch, I. Herraiz-Cardona, E.M. Ortega, J. García-Antón, V. Pérez-Herranz, *Chem Eng Trans*, 32 (2013) 865-870.
65. W.H. Baldwin, *J Chem Educ*, 8 (1931) 1749-1761.
66. J.L. Marshall, V.R. Marshall, <http://www.chem.unt.edu/~jimm/REDISCOVERY%207-09-2018/Hexagon%20Articles/nickel.pdf> 2014, pp. 11-17.
67. D. Stewart, <https://www.chemicool.com/elements/nickel.html>, Chemicool, 2019.
68. Mindat.org, <https://www.mindat.org/min-2895.html> 2019.
69. A.J. Bard, L.R. Faulkner, *Electrochemical methods: Fundamentals and applications*, JOHN WILEY & SONS, INC, New York, 2000.
70. Y. Cao, H. Liu, X. Bo, F. Wang, *Sci. China Chem*, 58 (2014) 501-507.
71. E.R. Llobet, J.Y. Nam, J.C. Tokash, A. Guisasaola, B.E. Logan, *Int J Hydrogen Energy*, 38 (2013) 2951-2956.
72. D.F. Call, M.D. Merrill, B.E. Logan, *Environ Sci Technol*, 43 (2009) 2179-2183.
73. K.-Y. Kim, W. Yang, B.E. Logan, *Environ Sci Technol*, 52 (2018) 7131-7137.
74. A.W. Jeremiasse, J. Bergsma, J.M. Kleijn, M. Saakes, C.J.N. Buisman, M.C. Stuart, H.V.M. Hamelers, *Int J Hydrogen Energy*, 36 (2011) 10482-10489.
75. I. Satar, W.R.W. Daud, B.H. Kim, M.R. Somalu, M. Ghasemi, M.H.A. Bakar, T. Jafary, S.N. Timmiati, *JTICE*, 89 (2018) 67-76.
76. L. Lu, D. Hou, Y. Fang, Y. Huang, Z.J. Ren, *Electrochimica Acta*, 206 (2016) 381-387.

77. M.F. Manuel, V. Neburchilov, H. Wang, S.R. Guiot, B. Tartakovsky, J Power Sources, 195 (2010) 5514-5519.
78. H. Hu, Y. Fan, H. Liu, Int J Hydrogen Energy, 42 (2009) 8535-8542.
79. A. Kellenbergera, N. Vaszilcsin, W. Brandl, N. Duteanu, Int J Hydrogen Energy, 32 (2007) 3258-3265.
80. F. Yang, K. Cheng, X. Xue, J. Yin, G. Wang, D. Cao, Electrochimica Acta, 107 (2013) 194-199.
81. E.K. Rideal, J Am Chem Soc, 42 (1920) 94-105.
82. F. Li, W. Liu, Y. Sun, W. Ding, S. Cheng, Int J Hydrogen Energy, 42 (2017) 3641-3646.
83. Y. Wang, W.Q. Guo, D.F. Xing, J.S. Chang, N.Q. Ren, Int J Hydrogen Energy, 39 (2014) 19369-19375.
84. G.C. Bond, Platinum Metal Rev, 12 (1968) 100-105.