Reaction kinetics for microbial-reduced mediator in an ethanol-fed microbial fuel cell

Evelyn^{1}, Edy Saputra^{1*}, Amun Amri¹, Aaron Marshall², and Peter Gostomski²*

¹Department of Chemical Engineering, Universitas Riau, Pekanbaru, Indonesia

²Department of Chemical and Process Engineering, University of Canterbury, Christchurch, New Zealand

Abstract. Microbial fuel cell (MFC) is an emerging energy production technology which converts the chemical energy stored in biologically degradable compounds to electricity at high efficiency. MFC with added mediator can enhance the electron transfer from the microbes to the anode, and used to treat industrial waste gases. In this work, the rate of microbial-reduced mediator reaction at the surface of glassy carbon (GC) electrode in an ethanol-fed MFC was investigated using cyclic voltammetry (CV), and compared with linear sweep voltammetry (LSV). The CV method provided a better estimation of the kinetic parameters than the LSV method due to low concentrations of the mediators used (0.2-1.0 mM), affecting the Tafel behaviours. All of the voltammograms indicated a quasi-reversible process for the anode reaction. The highest exchange current density (i_0) of 0.14 ± 0.01 mA/cm² and the highest power output of 0.008 mW/cm² were obtained using 0.2 mM N',N',N',N'-TMPD as the mediator. The MFC power density of 0.03 mW/cm² was achieved for 1 mM N-TMPD. Further increase in the power density (0.16 mW/cm²) was possible with carbon cloth electrode. The results of this study confirmed the advantage of a mediator for gaseous pollutant treatment and electricity production in a MFC.

1 Introduction

Increase in world population and economic development are leading to a rapid increase in energy demand. Fossil fuel-derived energy is limited in supply and will one day be depleted. Many forms of energy production are not sustainable, and increasing potential threat of climate change and global warming indicate a need to develop renewable and carbon-neutral energy production. The development of bio-electrochemical reactors based on microbial fuel cells (MFCs) represents an attractive technology for generating electricity using a wide variety of substrates, varying from pure organic compounds to complex organic waste [1, 2].

To date, MFCs still produce low power outputs (≤ 6 W/m² and/or ranging from 100 - 1000 W/m³) that limit their use in real applications [3-6]. The production of power depends on many components involved in the MFC i.e. microbial type, an anode, cathode,

* Corresponding author: evelyn@eng.unri.ac.id; edy.saputra@eng.unri.ac.id

electrolyte, and ion-exchange membrane (if used). Additionally, many factors influence its performance such as temperature, pH, nutrients and fuel cell configuration. Scaling up of an MFC will require a better understanding of all components and conditions to enable detection of the bottlenecks and improve the power outputs.

A slow electron transfer (ET) from microbes to the anode limits the power output in an MFC. The slow electron transfer is due to the positive energy needed to activate the oxidation-reduction reaction on the electrode surface, which causes a transfer resistance and hence potential losses (often called activation polarization). Several ways to overcome the activation polarization in the anode are by physical contact between bacterial cells and electrode surface or biofilm establishment, by diffusion of soluble mediator that shuttles electrons between the active site of redox enzymes in cells and electrode surface, or by conduction through molecular pili (nanowires) that channel cells to electrode surface [7]. It has been demonstrated that artificial mediators can improve the amount of energy obtained in an MFC [8-10]. However, the use of a redox mediator in the MFCs treating wastewater can create significant drawbacks such as difficulty in recovering the expensive and potentially toxic compound, thus does not attract considerable interest among researchers working in liquid-phase waste treatment. On the contrary, utilizing a redox mediator in the MFC treating gaseous pollutants is possible, since the soluble mediator would remain in the anode chamber as the gas flows through the reactor. Hence, there is potential integration between an MFC and anaerobic biofiltration system, in which the anoxic biofiltration removes gaseous contaminant and produces a stream of reduced mediator, followed by generation of electricity and production of a stream of oxidized mediator in the MFC [11]. To date, only a few studies that reported on the effectiveness of an MFC with the proposed scheme [12, 13].

Glassy carbon (GC) is an attractive carbon-based electrode for studying electro kinetics because it is inexpensive, inert in most electrolytes, and can be used over a wide potential range [14]. The electrode can easily be activated and maintained by carefully abrasion with emery paper and polishing in alumina slurries, and final cleaning by sonicating in water [15]. The activation levels of a GC electrode can be seen by observing the difference in the peak potential for a redox couple, for example, 60 mV for ferri/ferrocyanide redox systems [16]. This technique is simple and allows the determination of the actual surface area of the electrode [17]. Carbon cloth (CC) is another carbon-based electrode with relatively high surface areas. Many research groups have used carbon cloth as the materials for the anodes of MFCs to improve the power output per unit volume of reactor [18-20].

Therefore in this study, mediator reactions on a GC electrode in an ethanol-fed MFC was carried out, and the objectives were: (i) to compare the rate of oxidation-reduction of ferricyanide, thionine, and N',N',N',N'-TMPD using cyclic voltammetry, (ii) to compare the power density generated in the mediated-MFCs using linear sweep voltammetry, and; (iii) to compare the power density using GC and CC electrodes. Estimation of the kinetic parameters along with analyzing the power density would allow a better understanding of the behavior of three selected mediators for enhancing the electron transfer in an MFC.

Cyclic Voltammetry (CV) and Linear Sweep Voltammetry (LSV) have been commonly exploited to describe the thermodynamics of redox processes and the kinetics of electron transfer reactions. Regarding LSV, the potential of the working electrode is usually scanned in one direction only i.e. oxidation or reduction. With respect to CV, a further scan of potential in reverse direction is taken back to its original value, and the scan can be continued to the forward scan again to make a few repeated cycles. CV offers a fast determination of redox potential (E_o) of the analyte, which provides information about the cathodic and anodic potential (E_{pc} ; E_{pa}) and the cathodic and the anodic peak current (I_{pa} ; I_{pc}). From these, separation between peak potentials (ΔE_p), shift of E_{pc} and E_{pa} values during the timescale of experiments; ratio of the peak currents (I_{pa}/I_{pc}), current as a

function of scan rate (I_p vs $v^{1/2}$) are obtained, and can be used to determine the electrochemical reversibility of a redox couple i.e. mediator.

Kinetics of electrochemical reactions is often reported in the term of exchange current density (i_0 in mA/cm^2) and rate constant (k_0 in cm/s). The i_0 value depends on the concentration of electroactive chemical species at the anode surface, reaction, and surface of the electrode where the reaction occurs. Several equations have been proposed to calculate k_0 based on ΔE_p (hence, the i_0) [21-23]. Among them is Nicholson and Shain's method through the utilization of a dimensional parameter value (ψ) as the function of ΔE_p according to the following equations (Eq. 1 and 2):

$$k_0 = \Psi \left[\frac{\pi a D_{ox}}{\gamma} \right]^{1/2} [v]^{1/2} \quad (1)$$

$$\gamma = \left[\frac{D_{ox}}{D_{red}} \right]^{1/2} \quad (2)$$

where g is the diffusion coefficient ratio of the oxidized and reduced mediator, and a is the electron transfer coefficient which can be determined. Following this, reversibility factor (L) is defined (Eq. 3): for reversible reactions; for quasi-reversible reactions, and; for irreversible reactions [24].

$$L = \frac{k_0}{(\pi D_0 \frac{nF}{RT} v)} \quad (3)$$

Tafel slope (b value in V) can also be used to analyze the performance of an electrode reaction through determination of the exchange current density or i_0 by linear regression at overpotentials between 60 mV and 100 mV [25, 26]. The Tafel slope is a simplification of Butler–Volmer Equation in Eq. 4 at high overpotential (η in V) (Eq. 5). The value of the Tafel slope is also given by Eq. 6.

$$i = i_0 \left[\exp \frac{\alpha_A z F \eta}{RT} - \exp \frac{(-\alpha_C z F \eta)}{RT} \right] \quad (4)$$

$$\eta_{act} = b \log \left(\frac{i}{i_0} \right) \quad (5)$$

$$b = \left(\frac{2.303 RT}{\alpha n F} \right) \quad (6)$$

where i is the applied current density (mA/cm^2), η_{act} is the activation overpotential, F is Faraday constant (C/mol), and n is the number of electrons transferred, R is the universal gas constant ($\text{J}/\text{mol K}$), and T is the absolute temperature (K).

The Tafel method has been previously used for analysis and comparison of different anode/cathode materials or different catalysts [20, 26]. All of the above equations enable the determination of kinetics parameters thus the rate of oxidation-reduction of a mediator on electrode surface along with generation of power density for an MFC.

2 Materials and methods

2.1 Microorganisms and culturing

Acetic acid bacteria identified as *Acinetobacter calcoaceticus* (Macrogen, Korea), was isolated from compost using medium enriched with ethanol as a sole carbon source. The medium had the following composition (per litre of deionized or DI water): NaNO₃, 2 g; MgSO₄·7H₂O, 0.4 g; CaCl₂·2H₂O, 0.1 g; FeSO₄·7H₂O, 0.003 g; KCl, 0.12 g; KH₂PO₄, 0.48 g; Na₂HPO₄·12H₂O, 0.55 g, and EDTA disodium salt, 0.00186 g. 1 mL trace elements were also added (per litre): MnCl₂·4H₂O, 0.02 mg; ZnSO₄·7H₂O, 0.07 mg; NiCl₂·6H₂O, 0.02 mg; CoCl₂·6H₂O, 0.1 mg; CuCl₂, 0.01 mg; NaMoO₄·2H₂O, 0.03 mg; H₃BO₃, 0.02 mg. The medium was sterilized by autoclaving. After cooling, 2.6% (v/v) of ethanol solution and 0.1 g of cycloheximide was added into the 1 L sterile medium (pH = 6.5). A 250 mL Erlenmeyer flask was used to grow the aerobic batch cultures at room temperature. The incoming air passed through an initial flask containing a similar amount of ethanol to minimize ethanol evaporation in the growth flask [27]. A dry cell weight of 0.8-1 g/L was used for all MFC experiments.

2.2 Redox mediators

Thionine acetate [TH] and potassium ferricyanide [FR] were purchased from Sigma-Aldrich, whereas N'-N'-N'-TMPD [N-TMPD] was kindly supplied by the Chemistry Department at the University of Canterbury, New Zealand. The stock solutions of the mediators were prepared by completely dissolving in DI water, and the required mediator concentration was made by diluting the stock solution into the growth medium.

2.3 MFC system construction

A conventional double-chambered microbial fuel cell was made as previously described [28]. Both of the anode and cathode compartments had a total volume of 25 mL and were separated by a proton exchange membrane (PEM, Nafion 212) with the surface area of 4.15 cm². The PEM was pretreated by boiling in a 30% H₂O₂ solution and followed by boiling in 0.5 M H₂SO₄, each for 1 hr, and then stored in DI water before being used [29]. The anodes and the cathodes used in the study were either glassy carbon (0.071 cm²) or carbon cloth (2 cm²). All of the electrodes were pre-treated or were replaced with a new one (for CC) before use. GC was pretreated by polishing with 0.3 and 0.05 µm alumina slurry and successive washing until a mirror-like finish was obtained, followed by sonicating in deionized water for 3 minutes before use. Cathodic compartment contained a 50 mM FR in 1 M phosphate buffer (PBS) solution to avoid significant polarization at the cathode. A saturated calomel reference electrode (SCE) was used as a reference electrode for all reported values in this study.

2.4 MFC characterization using Linear Sweep Voltammetry (LSV) and Cyclic Voltammetry (CV)

All electrochemical measurements were conducted using a DY2100 Multi-Potentiostat (Digi-Ivy, Inc. Austin, TX) connected to a PC. Before MFC characterization, the anodic compartment was inoculated with a suspension of *A. calcoaceticus* into the medium containing 2.6% (v/v) ethanol. Argon was continuously sparged in the anodic compartment to maintain the anoxic conditions. Then, the mediator (0.2 or 1 mM) was added to the

growth medium. The LSV and CV scans were started when the mediator had been fully reduced by the bacteria (determined by color's observation). CV measurements were performed at different scan rates (0.01 V/s, 0.05 V/s and 0.1 V/s) and several cycles in the anodic and cathodic direction within a range of potential where the redox molecule peaks were seen (-0.2 V to 0.7 V). Then, the important CV parameters were extracted from the voltammograms to compare the three mediators used. For the calculation of k_0 , γ values of 1.04 for FR and 1.0 for TH and N-TMPD were used (determined in preliminary experiments). LSV measurements were carried out at a scan rate of 1×10^{-4} V/s from the open circuit voltage (OCV) until the mass transfer limited current was reached. The voltage and power density curves were generated from the difference in the anodic and cathodic polarization curves and used to obtain the power density data. Tafel parameters were obtained from the polarization curves at overpotential regions < 0.2 V when the Tafel behaviors were observed.

3 Results and discussion

3.1 Characterization of mediator using cyclic voltammetry

Fig. 1 presents the voltammograms of the microbial-reduced mediators (Ferricyanide, Thionine, and N-TMPD) at 0.01 V/s, 0.05 V/s, and 0.1 V/s on the GC electrode. Generally, all of the mediators showed electrochemically active behaviors by cyclic voltammetry, in which there were oxidation and reduction peaks observed in the voltammograms. The presence of ethanol degrading bacteria in the solution modified the shape of the voltammograms. Initially, when only mediator presence in the analyte, all of the voltammograms for the three mediators showed a reversible redox process i.e. ΔE_p values were around 59 mV and 30 mV for one electron and two electrons transfer, respectively (not shown). In the presence of bacteria, the peak separation (ΔE_p) values were greater than 59/n mV for the three mediators with the values increased with increasing scan rates (v) (Table 1), suggesting that the processes were not completely reversible anymore or quasi-reversible processes [24]. The curves also showed larger peaks for the reduction than for the oxidation. It seemed that the bacteria decreased the amount of the reduced and the oxidized mediator available at the surface of the electrode, decreasing the level of electrons flowed from the mediator to the electrode within the time frame of applied potentials. The quasi-reversible reaction means that the redox reactions were not fast enough to maintain the concentration of the oxidized and reduced mediator at the surface of the GC electrode as required by the Nernst Equation [23]. The same behaviors have also been reported for the voltammetric interactions of different mediators in the presence of *Rhodobacter sphaeroides* [30].

The kinetics of an electrochemical reaction is determined by the charge transfer process ($O + ne^- = R$) and mass transfer (diffusion) of electroactive species. A fast charge transfer indicates a reversible process. Regarding a quasi-reversible process, the electron transfer is influenced partly by charge transfer and partly by diffusion of electroactive species [31]. It can be seen from Table 1 that there were in proportional increases in the peak currents with the square root of v , which is an indication of both charge transfer and diffusion controlled reaction. The ratios of the peak currents (I_{pa}/I_{pc}) were also not equal to 1 for all mediators, suggesting that not all of the mediators reduced in the forward scan were available to be reoxidized in the backward scan, or reverse. In other words, the equilibrium values of the oxidized and reduced mediator cannot be maintained at the surface of the GC electrode. When the peak current ratio is not equal to unity, the process is quasi-reversible [32].

Fig. 1. Cyclic voltammograms of microbial-reduced mediators at three different scan rates on GC electrode: 0.2 mM FR, 0.2 mM TH, 0.2mM N-TMPD, and 1 mM N-TMPD.

E_{pa} values become more positive and E_{pc} values become more negative (or increasing ΔE_p values as the v increases) during the timescale of experiments is also in agreement with the criteria for quasi-reversible process [33]. The shifting of E_p was observed for FR and N-TMPD voltammograms (Table 1). In TH system, the E_{pa} becomes more negative i.e. from -0.09 V to -0.098 V at 0.1 V/s, although the ΔE_p kept increasing with increasing scan rates (0.049 V to 0.061 V). According to Zanello [33], care should be taken when the shift of E_p values results from uncompensated solution resistance. However, the problem can be overcome by increasing the concentration of the analyte. Nonetheless, the quasi-reversible processes were still seen with 1 mM of N-TMPD (Fig. 1). Further investigation

would be needed such as obtaining the kinetics information with higher scan rates (> 0.1 V/s) for a better understanding of the system.

Based on the voltammograms in Fig. 1, the anode reaction using N-TMPD as the mediator showed the best performance among the mediators used despite its broader peaks. The highest oxidation currents were achieved with a similar concentration of 0.2 mM due to the two-step redox processes i.e. a total of 48.7×10^{-3} mA/cm² compared to 30.8×10^{-3} mA/cm² and 46×10^{-3} mA/cm² for FR and TH respectively, at the scan rate of 0.1 V/s (Table 1). As the N-TMPD concentration was increased five times, the current was also increased more than four times (215×10^{-3} mA/cm²). The voltammograms with N-TMPD gives two reversible oxidation-reduction peaks according to the reactions in Eq. 7 and 8. The two peaks were observed at 0.12 V and 0.47 V vs. SCE, respectively [34, 35]. The first oxidation peak ($E_{o_1} = 0.12$ V) was also similar to the value reported by [36].

Table 1. Cyclic voltammetric data for microbial-reduced mediators on GC electrode.

v (V/s)	E_{pa} (V)	E_{pc} (V)	$\Delta E_p/n$ (V)	E_o (V)	$I_{pa} \times 10^{-3}$ (mA/cm ²)	$I_{pc} \times 10^{-3}$ (mA/cm ²)	I_{pa}/I_{pc}
FR (0.2 mM)							
0.01	0.2130	0.140	0.073	0.177	10.2	-14.3	0.71
0.05	0.217	0.135	0.082	0.176	15.8	-22.8	0.69
0.10	0.224	0.120	0.104	0.172	30.8	-40.4	0.70
TH (0.2 mM)							
0.01	-0.100	-0.149	0.049	-0.122	3.12	-3.55	0.88
0.05	-0.090	-0.140	0.050	-0.115	10.5	-13.2	0.80
0.10	-0.098	-0.158	0.061	-0.128	46	-57	0.81
N-TMPD (0.2 mM)							
0.01	0.157	0.080	0.077	0.12	5.1	-6	0.85
	0.498	*	-	-	15.4	-	-
0.05	0.158	0.078	0.080	0.12	14.4	-12.5	1.15
	0.500	*	-	-	26.4	-	-
0.10	0.16	0.068	0.092	0.11	17	-19.2	0.89
	0.503	*	-	-	31.7	-	-
N-TMPD (1.0 mM)							
0.01	*	*	*	*	*	*	*
0.05	0.180	0.077	0.103	0.129	67	-55	1.21
	0.500	0.425	0.075	0.463	85.3	-97	0.88
0.10	0.182	0.075	0.107	0.129	85	-71	1.20
	0.505	0.420	0.085	0.463	130	-149	0.87

* too broad to be determined.

3.2 Rates of anode reactions on GC electrode

Table 2 shows the kinetic parameters for the 0.2 mM mediators on the GC electrode. The highest average k_o value at 0.1 V/s of 6.4×10^{-3} cm/s was obtained with N-TMPD compared to 4.8×10^{-3} cm/s and 2.7×10^{-3} cm/s for FR and TH mediator, respectively (estimated from the values). Rogers et al. [35] reported lower k_o values (2.6 to 7×10^{-3} cm/s with 2 mM to 9 mM of N-TMPD). However, a platinum electrode was used vs. GC in this study. Further increase in the k_o value ($= 8.3 \times 10^{-3}$ cm/s) with 1.0 mM N-TMPD was observed due to the two-step redox reactions, giving the highest i_o value of 0.8 mA/cm². It is desired for an electrode reaction to have a high i_o as an indicator of a fast reaction rate and lower activation barrier. The i_o value obtained in this study with 1 mM N-TMPD was more than ten times higher than the i_o value obtained by Lowy and Tender [25] i.e. 0.8 mA/cm² vs. 0.06 mA/cm² using 50 mM AQDS modified electrode. The i_o value was also higher than mediatorless and pretreated GC, carbon fiber, or graphite ceramic containing Ni²⁺ and Mn²⁺ anode in past studies (0.003 mA/cm² to 0.10 mA/cm²) [37, 38].

Table 2. Kinetic parameters for three mediators on GC electrode.

v (V/s)	α	b (V decade ⁻¹)	ψ	$k_o \times 10^{-3}$ (cm/s)	i_o (mA/cm ²)	A
FR (0.2 mM)						
0.01	0.51	0.116	1.810	5.2	0.10	3.1
0.05	0.50	0.118	1.052	6.7	0.13	1.8
0.10	0.50	0.118	0.510	4.8	0.09	0.9
TH (0.2 mM)						
0.01	0.55	0.054	0.602	1.6	0.06	1.1
0.05	0.50	0.059	0.568	3.4	0.13	1.0
0.10	0.50	0.059	0.312	2.7	0.10	0.6
N-TMPD (0.2 mM)						
0.01	0.52	0.114	1.362	3.8	0.07	2.4
0.05	0.53	0.111	1.140	7.0	0.14	2.0
0.10	0.46	0.128	0.723	6.4	0.12	1.3
N-TMPD (1.0 mM)						
0.01	-	-	-	-	-	-
0.05(1,2)	0.50	0.118	0.525	3.3	0.32	0.9
	0.51	0.116	1.500	9.5	0.91	2.7
0.10(1,2)	0.51	0.116	0.574	4.2	0.41	0.8
	0.51	0.116	0.920	8.3	0.80	1.6

The Nicholson and Shain’s Equation enabled determination of reversibility (L) for the redox couples (Table 2). All of the L values declined with the scan rates, suggesting a shift from reversible behavior. This result is in agreement with previous indicators. As the value increases, the process approaches a reversible behavior, thus fast kinetics [39].

As expected, the calculated Tafel slope from Eq. 6 (based on their α values) was found at around 0.118 V per decade for FR and N-TMPD for a single electron transfer, whereas the value of 0.059 V per decade was found with TH mediator for two-electron transfer reactions (Table 2). The obtained α values were all close to 0.5, suggesting the activation

barriers lies between the products and the reactants as the voltage was applied in the redox reactions [40]. Tafel parameters from LSV method were difficult to obtain due to the low concentrations of the mediators used causing mass transfer limitations at fairly low overpotentials (~100 mV).

3.3 Microbial fuel cell performance

Table 3 summarizes the performance of mediated MFCs in this study. The data were collected by using the LSV method and were derived from the differences in the cathodic and anodic polarization curves. The results suggest that N-TMPD was the best mediator for the ethanol-fed MFC. The highest power densities of 0.03 mW/cm² were achieved with the GC electrode. Katz et al. [41] reported a short circuit current (sc) and a cell voltage of 0.18 mA/cm² and 0.53 V, respectively, when using 2-hydroxy-1,4-naphthoquinone (HNQ) with GC electrode in a glucose-fed MFC. The sc and a cell voltage of 0.172 mA/cm² and 0.49 V, respectively, are comparable to those study. Carbon cloth (CC) electrode results obtained in our studies showed a higher power density [9], reaching 0.09 mW/cm² for 0.2 mM and 0.16 mW/cm² for 1.0 mM of N-TMPD [9]. To conclude, the combination of a gaseous substrate with a mediator in an MFC offers a significant promise for gaseous pollutant treatment and electricity generation.

Table 3. Microbial fuel cell performance for three selected mediators on GC electrode.

Anode	Mediator	Power density (mW/cm ²)	Reference
GC	Without mediator	0.001	This study
	0.2 mM FR	0.001	
	0.2 mM TH	0.005	
	0.2 mM N-TMPD	0.008	
	1 mM N-TMPD	0.030-0.172 mA/cm ² (sc) 0.49 V	
GC	0.5 mM HNQ	0.18 mA/cm ² (sc) 0.53 V	[41]

4. Conclusions

In summary, voltammograms indicated that the anode reactions on glassy carbon are quasi-reversible processes for all mediators, which were shown by the peak separation values (ΔE_p) greater than 59/n mV, in proportional increases in the peak currents with the scan rates (v), shifts of E_{pa} (become more positive) and E_{pc} values (become more negative) with the scan rates, ratios of the peak currents (I_{pa}/I_{pc}) ≠ 1, and decreases of the L values with the scan rates. CV method provided a better estimation of the kinetic parameters of microbial-reduced mediator reactions than linear sweep voltammetry (LSV) method due to the low concentrations of mediators used, affecting the Tafel behaviors. Glassy carbon is a suitable anode material for studying electrokinetics of mediator reaction due to its distinct surface area and easier activation procedures. N-TMPD exhibited the best performance among all of the mediators used in the ethanol-fed MFC. The highest average k_o value of 6.4x10⁻³ cm/s was obtained with N-TMPD compared to 4.8x10⁻³ cm/s and 2.7x10⁻³ cm/s for FR and TH, respectively, at similar concentration (0.2 mM). Increasing the concentration of mediator increased the exchange current (i_o), with the highest current density obtained at 0.8 mA/cm² using 1 mM N-TMPD. The highest power output achieved with this mediator

on GC electrode was 0.03 mW/cm^2 . The use of high surface area material such as carbon cloth could improve the power density up to 0.16 mW/cm^2 .

References

1. B.E. Logan, Environ. Sci. Technol. **38** (2004)
2. K. Rabaey, P. Clauwaert, P. Aelterman, W. Verstraete, Env. Sci. Tech. **39** (2005)
3. D. Xing, Y. Zuo, S. Cheng, J.M. Regan, B.E. Logan, Env. Sci. Tech. **42** (2008)
4. M. Rahimnejad, A. Adhami, S. Darvari, A. Zirepour, S. Oh. Alexandria Eng. J. **54** (2015)
5. F. Zhao, R.C.T. Slade, J.R. Varcoe, Chem. Soc. Rev. **38** (2009)
6. Y. Zuo, D. Xing, J.M. Regan, B.E. Logan, Appl. Env. Microbiol. **74** (2008)
7. X. Xie, L. Hu, M. Pasta, G.F. Wells, D. Kong, C.S. Criddle, Y. Cui, Nano Lett. **11** (2010)
8. S. Babanova, Y. Hubenova, M. Mitov, J. Biosci. Bioeng. **112**, 379-387 (2011)
9. E. Evelyn, Y. Li, A. Marshall, P. Gostomski, *Proc. of the Chemeca: Quality of Life Through Chemical Engineering New Zealand* (2012)
10. J. Sun, W. Li, Y. Li, Y. Hu, Y. Zhang, Bioresour. Technol. **142**, 407-414 (2013)
11. Evelyn, Y. Li, A. Marshall, P.A. Gostomski. Rev. Env. Sci. Biotechnol. **3** (2014)
12. C.H. Wu, J.C. Shih, C.W. Lin, Intl. J. Hydrogen. Energ. **41** (2016)
13. C.H. Wu, C.W. Lin, Engineers. **68** (2016)
14. V.F. Sturm, Angewandte Chemie **100** (1988)
15. A. Dekanski, J. Stevanović, R. Stevanović, B. Ž. Nikolić, V.M. Jovanović, Carbon **39** (2001)
16. S. Ranganathan, T.C. Kuo, R.L. McCreery, Anal. Chem. **71** (1999)
17. V.S. Bagotsky, *Fundamental of electrochemistry* (Jhon Wiley & Sons, New Jersey, 2006)
18. S. Cheng, B.E. Logan, Electrochem. Commun. **9** (2007)
19. J. Liu, Y. Qiao, C.X. Guo, S. Lim, H. Song, C.M. Li, Bioresour. Technol. **114** (2012)
20. K. Scott, I. Cotlarciuc, D. Hall, J. Lakeman, D. Browning, J. Appl. Electrochem. **38** (2008)
21. E. Gileadi, U. Eisner, J. Electroanal. Chem. **28** (1970)
22. R. J. Killinger, J.K. Kochi, J. Phys. Chem. **85** (1981)
23. R.S. Nicholson, I. Shain, Anal. Chem. **36** (1964)
24. A.J. Bard, L.R. Faulkner, *Electrochemical methods: fundamentals and applications* (Jhon Wiley & Sons, New York, 2001)
25. D.A. Lowy, L.M. Tender, J. Power Sources **185** (2008)
26. S. Freguia, K. Rabaey, Z. Yuan, J. Keller, Electrochim. Acta **53** (2007)
27. H. Eysseric, B. Gonthier, A. Soubeyran, G. Bessard, R. Saxod, L. Barret, Alcohol **14** (1997)
28. S.E. Oh, B.E. Logan, Appl. Microbiol. Biotechnol. **70** (2006)
29. K.J. Chae, M. Choi, F.F. Ajayi, W. Park, I.S. Chang, I.S. Kim. Energ. Fuels **22** (2008)
30. Agostiano, M. Caselli, P. Cosma, M.D. Monica, Electrochim. Acta **45** (2000)

31. E.R. Brown, R.F. Large. *Electrochemical methods* (Wiley, New York, 1971)
32. S. Karthikeyan, T.M. Arthikeyan, R. Rajendiran, R. Ajendiran, R. Kannapan, R. Mahalakshmy, P. Venkatesan, S. Rao, *Proc. Indian Acad. Sci.* (2001)
33. P. Zanello, *Inorganic electrochemistry: Theory, practice and application* (The Royal Society of Chemistry, UK, 2003)
34. R.G. Evans, O.V. Klymenko, P.D. Price, S. G. Davies, C. Hardacre, R.G. Compton, *Chem. Phys. Chem.* **6** (2005)
35. E.I. Rogers, D.S. Silvester, S.E.W. Jones, L. Aldous, C. Hardacre, A.J. Russell, S.G. Davies, R.G. Compton, *J. Phys. Chem.* **111** (2007)
36. G. Chaka, A. Bakac, *R. Soc. Chem.* **2** (2008)
37. J.L. Liu, D.A. Lowy, R.G. Baumann, L.M. Tender, *J. Appl. Microbiol.* **102** (2007)
38. Q. Wen, Y. Wu, L. Zhao, Q. Sun, F. Kong, *J. Biomed. Biotechnol.* **11** (2010)
39. H. Matsuda, Y. Ayabe, *Z. Electrochem.* **59** (1955).
40. R.G. Compton, C.E. Banks, *Understanding voltammetry* (World Scientific, Singapore, 2007)
41. E. Katz, A.N. Shipway, I. Willer, *Handbook of fuel cells-fundamentals, technology and applications* (John Wiley & Sons, New Jersey, 2003)