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Grey relational analysis for comparative assessment of different cathode materials in microbial electrolysis cells

Abudukeremu Kadier [a,*], Peyman Abdeshahian [b], Yibadatihan Simayi [c], Manal Ismail [a,d], Aidil Abdul Hamid [e], Mohd Sahaid Kalil [a]

[a] Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, National University of Malaysia (Universiti Kebangsaan Malaysia), 43600, Bangi, Selangor, Malaysia
[b] Department of Biochemical Engineering, Faculty of Chemical Engineering, Universiti Teknologi Malaysia, UTM Skudai, 81310, Johor, Malaysia
[c] Institute of Tropical Agriculture, University Putra Malaysia, 43400, UPM Serdang, Selangor, Malaysia
[d] Fuel Cell Institute, National University of Malaysia (Universiti Kebangsaan Malaysia), 43600, Bangi, Selangor, Malaysia
[e] School of Biosciences and Biotechnology, Faculty of Science and Technology, National University of Malaysia (Universiti Kebangsaan Malaysia), 43600, Bangi, Selangor, Malaysia

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ABSTRACT

MEC (Microbial electrolysis cell) is an emerging and promising bio-electrochemical process for sustainable production of hydrogen gas. The performance and cost of cathode materials are the most important factors in MEC. In order to enhance MEC performance and reduce the fabrication and operational costs of electrodes, a wide range of cathode materials have been developed and tested in the recent years. However, no standard and systematic analytical method has been developed to make a comparative assessment of the cathode materials in MECs. In this study, a statistical method, namely GRA (grey relational analysis) was exploited to evaluate hydrogen evolution performance of eight different non-precious metal alloy cathodes, including stainless steel alloys 304, 316, 420, A286, and nickel alloys 201, 400, 625 with Ni HX in comparison to precious metal of Pt (platinum). Statistical results revealed that materials tested were ranked based on the grey relational grade values as ASS 286 > Pt > SS 304 > Ni 625 > SS 420 > Ni HX > Ni 400 > Ni 201 > SS 316. The results obtained showed stainless steel A286 had the best efficiency in MEC test based on grey relational grade. This study indicated that GRA could be used as a novel method to assess the performance of cathodes in MEC.

1. Introduction

Global fossil fuel consumption has increased concurrently with the world population growth. On the other hand, greenhouse gas evolution has largely increased by the utilization of fossil fuels which has caused worldwide warming and air pollution. This has led to the utilization of alternative clean and renewable energy sources which reduce adverse effects of fossil fuels [1–3]. Hydrogen is a sustainable and environmental-friendly energy carrier which has a greater energy yield of 112 kJ/g, accounting for 2.75-fold higher than hydrocarbon fuels [4].

MEC (Microbial electrolysis cell) is a promising approach for H_2 production from a range of biodegradable substrates such as wastewater, VFAs (volatile fatty acids), biomass and a variety of renewable resources. In an MEC method, EAB (electrochemically active bacteria) grow on anode surface oxidize organic matter and generate CO_2, e^- (electron) and H^+ (proton) as a part of its metabolism. The bacteria transfer the electrons to the anode, while the protons are released directly into the MEC solution. Electrons generated then move through a wire to a cathode where they are combined with the free protons in solution. This reaction results in H_2 generation (Fig. 1). However, the combination of protons and electrons for the generation of hydrogen requires a cathode potential at least −0.414 V (vs NHE) at a pH value of 7 and temperature of 30 °C [5–8]. The reactions at the anode and cathode are shown below:

$$\text{Anode}: \quad CH_3COO^- + 4H_2O \rightarrow 2HCO^{3-} + 9H^+ + 8e^- \qquad (1)$$

$$\text{Cathode}: \quad 8H^+ + 8e^- \rightarrow 4H_2 \qquad (2)$$

These two reactions occur at biological conditions with a

* Corresponding author. Tel.: +60 186674104; fax: +60 389216148.
E-mail address: abudoukeremu@163.com (A. Kadier).

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Abbreviation & nomenclature

C_E	coulombic efficiency
EAB	electrochemically active bacteria
Eap	applied voltage (V)
GRA	grey relational analysis
HER	hydrogen evolution reaction
I_V	the volumetric current density (A/m^3)
MEC	microbial electrolysis cell
NHE	normal hydrogen electrode
Δmaxis	absolute maximum deviation value
Δminis	absolute minimum deviation value
$\Delta i(k)$	absolute deviation value
Q_{H_2}	volumetric hydrogen production rate
$r_{cat(H_2)}$	the cathodic hydrogen recovery
r_{H_2}	the hydrogen recovery
r_i	the grey relational grade
SS	stainless steel
S_i	standard deviation
$x_i(k)$	the standardization processing result
$x(k)$	the raw data
$\overline{X}$	mean of the same factor values

Greek letters

η_E	electricity efficiency
η_E	substrate efficiency
η_{E+S}	the overall energy efficiency
$\varepsilon i(k)$	The grey relational coefficient

pressure, temperature and pH value of 1 atm, 30 °C and 6.8–7, respectively.

Similarly, the production of renewable energy using electrochemical devices has been exploited in fuel cells [9]. Fuel cell is an electrochemical device which is consisted of two electrodes, known as cathode and anode inside an electrolyte. Hydrogen as fuel enters to the anode and oxygen is passed to the cathode. Hydrogen is split to negative and positive hydrogen ion (electron and proton) at the anode. Electron and proton obtained are then combined with oxygen at the cathode under electrochemical reaction to produce water [10]. In this regard, it has been indicated that hydrogen can act as long-term source of energy for fuel cells [11].

It has been found that MEC produces multifold hydrogen from biomass when compared with other conventional methods. In this view, low energy consumption is one of main advantages of this system over water electrolysis [12]. MEC has also superior advantages over the fermentative hydrogen production, such as higher hydrogen recovery [13,14] and more diverse substrate [15,16].

It has been shown that a number of factors affect the MECs performance including biological factors (type and source of microbial inoculums; electrogenic microorganisms), electrode materials and their properties, electron donors or substrate type and MEC reactor design. One of the key factors affecting the MEC performance and its application is the type of cathode for H_2 production, due to the large over-potential of the HER (hydrogen evolution reaction) on plain carbon electrodes [17]. A precious metal such as Pt (platinum) on the cathode has been used in most studies to catalyze HER, because precious metal catalysts can reduce cathode over-potential by lowering the activation energy [18]. However, the

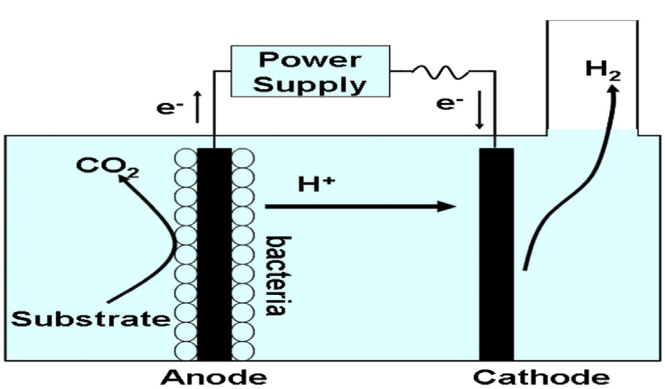

Fig. 1. Schematic of typical single chamber MEC construction and operation.

use of platinum as a cathode in MEC makes this process expensive, owing to high cost of platinum. Furthermore, the deleterious effect of chemicals such as sulphide as a common constituent of wastewater on platinum results in the reduced cathode efficiency [19].

Hence, practical implementation of MEC will mainly require operation at low cost. In this regard, it has been increasing interest to find other alternative cathode materials to make MEC technology economical and cost-effective.

Recently, plenty of studies have been performed on some low-cost platinum-free cathode catalysts such as molybdenum disulfide, tungsten carbide, and nickel alloys, namely NiMo, NiW and NiFeMo [20].

An attempt was made by Selembo et al. [21] who evaluated stainless steel alloys 304, 316, 420 and A286, and nickel alloys 201, 400, 625 and HX in MECs. They found that some of non-precious metal cathodes can be used in MECs to achieve hydrogen gas production rates better than those obtained with platinum.

A number of statistical approaches have already been developed to evaluate physico-chemical and biological processes. In this view, the generation of mathematical models has been taken into account based on the DOE (design of experiments). RSM (Response surface methodology) is a statistical method on the basis of DOE. RSM includes a series of statistical and mathematical techniques to define a model equation such a second-order polynomial model for the processes tested and to predict the response in relation to the model determined [22]. Moreover, RSM could be exploited to fit the model to the experimental data using different DOEs including central composite design [23] and Box-Behnken design [24]. DOE has also been applied for the development of the process model using Taguchi method [25]. In this method the effect of process parameters on the process conditions is evaluated to determine optimum conditions [26]. However, no statistical approach has already been exploited in the previous studies to compare the performance of different cathodes in MEC for hydrogen production.

GRA (Grey relational analysis) is an effective statistical method for measuring the degree of approximation among the sequences using a grey relational grade. It was developed by Deng [27]. GRA is an impacting measurement method in grey system theory that analyses uncertain relations between one main factor and all the other factors in a given system. It is actually a measurement of the absolute value of the data difference between sequences. It can be used to measure the approximate correlation between sequences with less data. Moreover, GRA can be applied for the analysis of many factors to overcome drawbacks and limitations associated with statistical methods [28]. The major advantage of GRA is that

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