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Short Communication

Hydrogen production in microbial electrolysis cells: Choice of catholyte

Siriporn Yossan [a], *Li Xiao* [b], *Poonsuk Prasertsan* [c,d], *Zhen He* [b,*]

[a] *Program of Science, Faculty of Liberal Arts and Science, Sisaket Rajabhat University, Sisaket 33000, Thailand*
[b] *Department of Civil Engineering and Mechanics, University of Wisconsin-Milwaukee, Milwaukee, WI 53211, USA*
[c] *Department of Industrial Biotechnology, Faculty of Agro-Industry, Prince of Songkla University, Songkhla 90112, Thailand*
[d] *Palm Oil Products and Technology Research Center (POPTEC), Faculty of Agro-Industry, Prince of Songkla University, Songkhla 90112, Thailand*

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ABSTRACT

A catholyte is a key factor to hydrogen production in microbial electrolysis cells (MECs). Among the four groups of catholytes investigated in this study, a 100 mM phosphate buffer solution (PBS) resulted in the highest hydrogen production rate of 0.237 ± 0.031 $m^3H_2/m^3/d$, followed by 0.171 ± 0.012 $m^3H_2/m^3/d$ with a 134 mM NaCl solution and 0.171 ± 0.004 $m^3H_2/m^3/d$ with the acidified water adjusted with sulfuric acid. The MEC with all catholytes achieved good organic removal efficiency, but the removal rate varied following the trend of the hydrogen production rate. The reuse of the catholyte for an extended period led to a decreasing hydrogen production rate, affected by the elevated pH. The cost of both the acidified water and the NaCl solution was much lower than the PBS, and therefore, they could be a better choice as an MEC catholyte with further consideration of cost reduction and chemical reuse/disposal.

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1. Introduction

Hydrogen is a promising alternative to fossil fuel and is considered as a clean fuel because its combustion generates no pollutants but water [1]. Hydrogen gas can be produced by both thermochemical (pyrolysis/gasification) and biological (biophotolysis, dark and photo fermentation) processes [2]. In recent years, a new method of hydrogen production has been developed based on bioelectrochemical principles in microbial electrolysis cells (MECs). The advantage of MEC technology is to produce hydrogen gas from a non-fermenting substrate (e.g., in wastewater) with a very low input of external energy. Therefore, MECs can function as an energy-efficient process for simultaneous waste treatment and energy (hydrogen) production.

Our understanding of MECs has been greatly advanced by intensive research on microbiology, substrates, and reactor configuration and operation [3,4]. MECs usually contain two chambers, an anode and a cathode separated by an ion exchange membrane (IEM). A single-chamber MEC was developed by omitting IEM to considerably simplify the reactor structure and potentially improve hydrogen production by

* *Corresponding author*. Tel.: +1 414 229 5846; fax: +1 414 229 6958.
E-mail address: zhenhe@uwm.edu (Z. He).
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reducing the MEC's internal resistance [5]. However, a great concern with the single-chamber MECs is methane production, which is caused by methanogens inhabiting the adjacent cathode and has been observed in several MECs including a pilot test [6]. Therefore, to produce high-purity hydrogen gas in an MEC, IEM may still be a preferable separator to prevent microbial contamination in the cathode. With an IEM and a separated cathode chamber, a simple but important question arises: what should be the catholyte?

A commonly used catholyte is a phosphate buffered solution (PBS), which can minimize the pH elevation and provide a certain electrolyte conductivity; however, the use of PBS may not be economical and environmentally friendly. The anode effluent (treated wastewater) could be a low-cost catholyte, which has been studied in microbial fuel cells (MFCs) [7], but it can introduce microorganisms including methanogens into the cathode chamber, resulting in methane production. Thus, we should avoid any catholytes containing microbial sources. In addition to PBS, several other catholytes have been studied, including salt solutions and bicarbonate buffers. In general, there is very limited information available about the comparison between these and other potential catholytes in terms of performance and cost. In this study, we aim to examine four different catholytes and provide suggestions on optimal choices of a catholyte in an abiotic cathode for sustainable hydrogen production in an MEC.

2. Materials and methods

2.1. MEC set up and operation

An MEC was made from two glass bottles, which were joined by a cation exchange membrane (Membranes International, Inc., GlenRock, NJ, USA). Each bottle had a liquid volume of 120 mL. The anode electrode was a carbon brush (Gordon Brush Mfg. Co., Inc., Commerce, CA, USA), and the cathode electrode was a piece of carbon cloth (Zoltek Corporation, St. Louis, MO, USA) with a length of 4 cm and a width of 3 cm. The cathode electrode was coated with Pt as a catalyst (0.5 mg Pt/cm^2) [8]. Both the anolyte and the catholyte were continuously mixed by magnetic stirrers. An external voltage (0.8 V) was applied to the circuit by connecting the negative pole of a power supply (3644 A, Circuit Specialists, Inc., Mesa, AZ, USA)

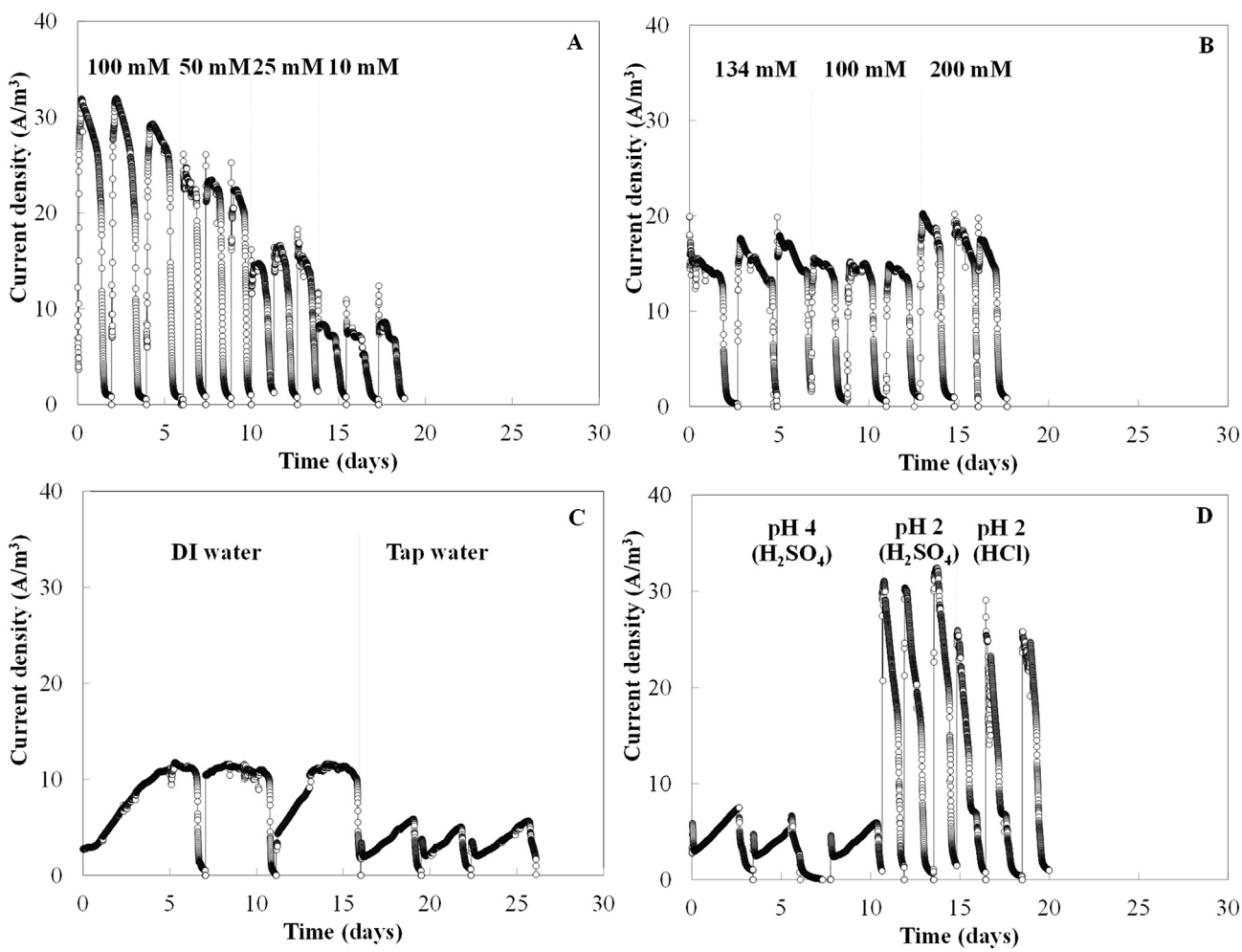

Fig. 1 – Current generation in the MEC with different catholytes: (A) 100, 50, 25 and 10 mM PBS; (B) 134, 100 and 200 mM NaCl; (C) DI and tap water; and (D) acidified water at pH 4 and pH 2 adjusted by H_2SO_4 or HCl.

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