Chemical Engineering Journal 258 (2014) 157–162

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

# Tetramethylammonium hydroxide production using the microbial electrolysis desalination and chemical-production cell

Guangli Liu, Haiping Luo *, Yaobo Tang, Shanshan Chen, Renduo Zhang, Yanping Hou

*Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology, School of Environmental Science and Engineering, Sun Yat-sen University, Guangzhou 510275, China*

## HIGHLIGHTS

- Tetramethylammonium hydroxide (TMAH) was produced using the MEDCC.
- The electricity consumption in the MEDCC was 0.76 kWh/kg TMAH.
- The electricity consumption in the MEDCC was 5–12% of that using electrodialysis.
- The mechanism of the synergistic reaction in the MEDCC was discussed.

## ARTICLE INFO

*Article history:*
Received 27 February 2014
Received in revised form 21 June 2014
Accepted 8 July 2014
Available online 27 July 2014

*Keywords:*
Tetramethylammonium hydroxide
Bioelectrochemical system
Energy consumption

## ABSTRACT

The aim of this study was to investigate the feasibility of tetramethylammonium hydroxide (TMAH) production using the microbial electrolysis desalination and chemical-production cell (MEDCC). With 1.0 g/L acetate in the anode chamber and tetramethylammonium chloride solutions with different concentrations in the desalination chamber, TMAH could be efficiently produced in the cathode chamber of MEDCC. With an applied voltage of 1.0 V, the concentration of TMAH reached 0.087 M within 17.5 h, with current efficiency of 52–58%. The electrical energy consumed for the TMAH production using the MEDCC was 0.76 kWh/kg, which was only 5–12% of that for the electrolysis and electrodialysis process. With the high value of TMAH produced in a friendly environment with low energy consumption, the MEDCC should be a potentially valuable method for the chemical production in practice.



## 1. Introduction

A bioelectrochemical system (BES) is an electrochemical device relying on the exoelectrogens to catalyze the anode and/or the cathode reactions [1]. Because the exoelectrogens can utilize many kinds of organics and release electrons in the neutral solution at room temperature, the BES is potentially useful in the electrosynthesis field [2]. Many products have been reported to be produced in the BES, such as hydrogen, hydrogen peroxide, methane, and others [3–6]. However, the application of BES is still limited mainly because of relatively low values of the above products. As demonstrated by Logan and Rabaey [7], high valuable products, such as alkali, may boost the application of BES.

Because of low decomposition temperature, harmlessness for silicon materials, and low toxicity, tetramethylammonium hydroxide (TMAH) has been widely used in the industries of electronics, organosilicone syntheses, and semiconductor production as an etching solution or catalyst [8]. Different methods have been developed to produce TMAH, mainly including precipitation, ion-exchange resin, electrolysis, and electrodialysis with bipolar membrane (EDBM) [9–13]. The precipitation method is based on the reaction between tetramethylammonium chloride (TMAC) and silver oxide to produce TMAH and a precipitate of silver chloride [9]. Nevertheless, applications of the precipitation method are limited by the high cost of silver oxide and heavy metal residue in the product. In the ion-exchange resin method, TMAH is produced through exchange $OH^-$ with $Cl^-$ from TMAC. Large amount of pure acid and alkali is required to regenerate the resin [10]. TMAH can also be produced with electrolysis to electrolyze a halogenated salt of quaternary ammonium [11]. In the anode of electrolysis cell, halogen ions become halogen gas, which is harmful for the anode electrode and catalysts (e.g., platinum) in the electrode. Halogen gas can also deteriorate the cation-exchange membrane in the electrolysis. To avoid any environmental risk, post-treatment procedure is required to collect hydrogen produced in the cathode [12]. Moreover, the energy consumption in the electrolysis cell is high (6.0 kWh per kg TMAH) [13]. With an applied voltage as

* Corresponding author. Tel.: +86 20 84110052; fax: +86 20 84110267.
*E-mail address:* luohp5@mail.sysu.edu.cn (H. Luo).

http://dx.doi.org/10.1016/j.cej.2014.07.025
1385-8947/

low as 0.814 V and the bipolar membrane, the rate of water dissociation into $OH^-$ and $H^+$ can be $5 \times 10^7$ times higher than that in the natural water dissociation process [14]. Therefore, TMAH can be produced using the EDBM based on the reaction of $OH^-$ from water dissociation with tetramethylammonium ions in TMAC. Without producing halogen and hydrogen gases, EDBM is considered as an environmental friendly technology. Nevertheless, the energy consumption in EDBM is still high (2.37–4.86 kWh per kg TMAH) [9]. Therefore, it is necessary to develop environment friendly methods for TMAH production with lower energy consumption.

In our previous work, a new type of BES, called microbial electrolysis desalination and chemical-production cell (MEDCC), has been developed to desalinate seawater and product acid and alkali simultaneously [15]. In the MEDCC, sodium hydroxide is generated from the reaction of hydroxide ions produced in the cathode chamber and sodium ions, which are transferred from the desalination chamber through the cation exchange membrane (CEM). Since the value of TMAH is more than 40 times higher than that of sodium hydroxide, the production of TMAH should be more competitive [9,16]. The MEDCC is a promising process for the chemical production with low energy consumption because part of the energy is self-provided by exoelectrogens from the anode chamber. Therefore, the objective of this study was to investigate the feasibility of TMAH production using the MEDCC. The performance of the MEDCC was evaluated from effects of initial concentrations of TMAC and applied voltages on TMAH production, current efficiency, and electrical energy consumption.

## 2. Materials and methods

### 2.1. MEDCC setup

The MEDCC reactor was setup following [15]. A schematic structure of the MEDCC is shown in Fig. 1. The anode electrode was made of graphite brush and the cathode with platinum as catalyst was made as previously described [15]. Effective volumes of the anode chamber, the acid-production chamber, the desalination chamber, and the cathode chamber were 28, 7, 7, and 14 mL, respectively. Bipolar membrane (BPM, Fumasep-FBM, Fumatech, German), CEM (Ultrex CMI-7000, MI, USA), and anion exchange membrane (AEM, Ultrex AMI-7001, MI, USA) were installed successively to separate the anode, acid-production, desalination, and cathode chambers. The size of each membrane was 3 cm in diameter.

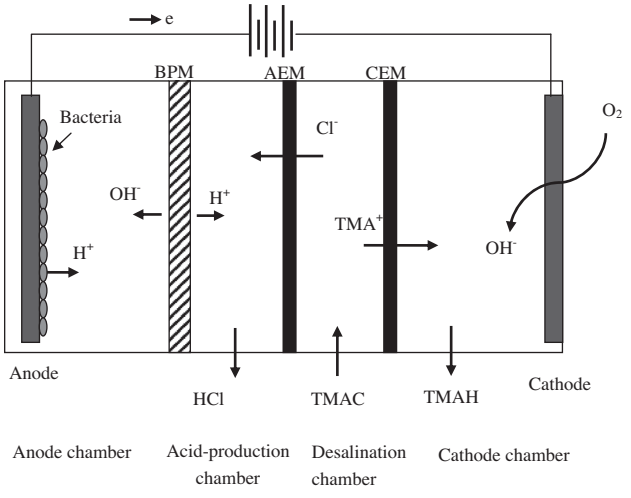


**Fig. 1.** Schematic structure of the MEDCC for TMAH production.

The anodic solution contained (in 1 L deionized water): 1 g $CH_3COONa$, 4.0896 g $Na_2HPO_4$, 2.544 g $NaH_2PO_4$, 0.31 g $NH_4Cl$, 0.13 g KCl, 12.5 mL trace metal solution, 12.5 mL vitamin solution, and the initial pH of the solution was adjusted to 7.0 [17]. To reduce the internal resistance of MEDCC, 1 g/L sodium chloride solution with the conductivity about 2.0 mS/cm was put into the acid-production chamber, and a TMAH (Sinopharm Chemical Reagent Co. Ltd., China) solution with the initial concentration of 0.01 M was used in the cathode chamber (pH = 12.0). Different TMAC (Sinopharm Chemical Reagent Co. Ltd., China) solutions in a range of 0.1 to 0.6 M were tested in the desalination chamber, with initial pH values of ~7.0. Four fixed voltages (0.6, 0.8, 1.0, and 1.2 V) were applied to the MEDCC circuit using a power supply (Itech, IT6700, China). An external resistance (10 Ω) was connected between the negative lead of the power supply and the cathode, and the positive lead of the power supply was connected to the anode. The solutions in all chambers were refreshed when the current density was below 0.4 $A/m^2$. The experiments for each treatment were carried out at 30 ± 1 °C in duplicate.

### 2.2. Analyses and calculations

The concentration of TMAH was determined using the titration method [9]. The chemical oxygen demand (COD) was measured using the dichromate standard method [18]. Solution conductivities and pH values were measured using a conductivity meter (Leici, DDS-11A, China) and a pH meter (Mettler Toledo, FE 20, Swiss), respectively.

Voltages cross the external resistance were recorded using a data acquisition system (model 2700; Keithley Instruments, Inc.). The voltage and external resistance were used to calculate the current. The current density ($A/m^2$) was estimated with the current normalized by the projected area of cathode electrode. The coulombic efficiency (CE) was calculated as described by Chen et al. [15]. The current efficiency (η) was determined as follows [9]:

$$\eta = 100\% \frac{zF(C - C_0)V}{\int_0^T Idt} \quad (1)$$

Here $z$ is the ion chemical valence ($z = 1$), $F$ is the Faraday constant (96,500 C equivalents$^{-1}$), $C_0$ and $C$ are the initial and final concentrations of TMAH in the catholyte (M), respectively, $V$ is the volume of the cathode chamber (L), $I$ the current in the circuit (A), and $T$ the operation time (s).

The total energy consumption in the MEDCC included the electricity input from the power supplier and the energy from acetate utilization by exoelectrogens in the anode chamber. Thus the total specific energy consumption (i.e., the energy consumption for the production of 1 kg TMAH, kWh/kg) was estimated with [19,20]

$$E = E_E + E_S \quad (2)$$

where $E_E$ and $E_S$ are the specific energy consumption from the electricity and the substrate removal (kWh/kg), respectively, and calculated by

$$E_E = \frac{\int_0^T UIdt}{3600(C - C_0)MV} \quad (3)$$

$$E_S = \frac{n_S \Delta H_S}{3600(C - C_0)MV} \quad (4)$$

Here $M$ is the TMAH molar weight (91 g/mol), $U$ the applied voltage on the MEDCC (V), $n_s$ the number of moles of substrate consumed during a batch cycle based on COD removal in the anode chamber (with a conversion factor of 0.78 g COD/g sodium acetate), and $\Delta H_s$ (870.28 kJ/mol) is the combustion heat of the substrate.