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# Electrosynthesis of glyceraldehyde by cyclic nano-MnO<sub>2</sub>/Mn<sup>2+</sup> in bipolar membrane-equipped electrolytic cell

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# 1. Introduction

GAD, a protective agent for blood glucose in medicine for its antiglycolytic effect, is by far one of the earliest discovered aldose compounds with optical activity [1]. A number of conventional methods for producing GAD have been reported, however, most were using strong oxidants with poor selectivity. One of the most promising technologies is selectively electrosynthesis using mild oxidation, a green chemistry and green engineering. For example,  $Mn^{3+}$  had been applied as the mild oxidant with high selectivity, but unstable and disadvantageous in transportation and storage [2,3].

In this paper, GAD was produced by the selective oxidation of the primary hydroxyl groups of glycerol, which was carried out in PAM/CMC BPM-equipped electrolytic cell using nano-MnO<sub>2</sub>/Mn<sup>2+</sup> as the cyclic and reproducible intermediate. Nano-MnO<sub>2</sub> was generated by the oxidation of Mn<sup>2+</sup> on the surface of the anode and served as a mild oxidant to convert glycerin to GAD selectively, meanwhile nano-MnO<sub>2</sub> was reversibly reduced to Mn<sup>2+</sup>, and thus the cyclic oxidation–reduction reaction was carried on throughout the entire electrochemical reaction. PAM/CMC BPM was applied as the separator in the electrolytic cell, which not only effectively prevented GAD from diffusing into the cathode chamber, but also played an important role in the supply of OH<sup>-</sup> to neutralize H<sup>+</sup> accumulated during the electrosynthesis.

# ABSTRACT

The composite PAM/CMC bipolar membrane (BPM) consisted of polyacrylamide (PAM) and carboxymethylcellulose (CMC) cross-linked by glutaraldehyde and Fe<sup>3+</sup>, respectively. The PAM/CMC BPM with high permselectivity and good thermal stability was then applied as a separator in the electrolytic cell for the electrosynthesis of glyceraldehyde (GAD) using nano-MnO<sub>2</sub>/Mn<sup>2+</sup> as the cyclic and reproducible intermediate. The cyclic nano-MnO<sub>2</sub>/Mn<sup>2+</sup> intermediate illustrated a good reversibility shown in the cyclic voltammetry. The cross-section SEM image of PAM/CMC BPM illustrated a laminate of a juxtaposed PAM layer joining to CMC layer with a clear interface. The yield of GAD approached 91.6% and the current efficiency reached 65.5%.

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# 2. Material and methods

#### 2.1. Materials

PAM  $(M_W{>}3{\times}10^6)$  and CMC (Na-content degree of 6.5%–8.5%) were purchased from Guoyao Chemicals Co. Ltd. Other chemicals used were of analytical grade.

## 2.2. Preparation of PAM/CMC BPM

In the two-step preparation of PAM/CMC BPM, a paste method was employed, a conventional method granting BPM high permselectivity and good mechanical strength.

Firstly, CMC sol (3.0 wt.%) together with a mixture of anhydrous ethanol and glycol was stirred at 20 °C for 3 h. Then CMC sol was casted on a glass plate and dried up in advance. Then the CMC layer was immersed in FeCl<sub>3</sub> solution (8.0 wt.%, 10 min) to incorporate a certain amount of Fe<sup>3+</sup>. According to the theory of Hanada [4], the transition region would result in a more hydrophilic interphase after penetrating heavy metal ions, formed a higher charge area around the transition metal, and reduced the voltage of electrolysis. Besides,  $-COO^-$  group in CMC was cross-linked by Fe<sup>3+</sup> to form an insoluble metal chelate, which would result in better mechanical and thermal properties.

Secondly, a certain amount of formaldehyde was added in PAM sol (3.0 wt.%, pH = 9–10) and stirred at 50 °C for 2 h. Then, dimethylamine was added and stirred at 20 °C for another 2 h ( $n_{PAM}$ : $n_{formaldehyde}$ :  $n_{dimethylamine}$ : $n_{HCI}$  = 1:1:1.2:1). The weak basic groups in PAM would enhance water dissociation by Simons' theory [5]. The modified PAM sol was casted onto CMC layer to form PAM layer. Finally, the composite

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PAM/CMC BPM was allowed to be totally dried at room temperature for around 2 days.

#### 3. Results and discussion

# 3.1. Reversibility of $MnO_2/Mn^{2+}$

The cyclic voltammetry for nano-MnO<sub>2</sub>/Mn<sup>2+</sup> was measured in Ar atmosphere with H<sub>2</sub>SO<sub>4</sub> electrolyte (0.5 mol L<sup>-1</sup>) in the cathode chamber and a mixture of MnSO<sub>4</sub> (0.5 mol L<sup>-1</sup>) and H<sub>2</sub>SO<sub>4</sub> (0.1 mol L<sup>-1</sup>) in the anode chamber. Graphite electrodes (apparent area = 5.0 cm<sup>2</sup>) were used as both the working electrode and the counter electrode while Ag/AgCl electrode as the reference electrode.

When the electrolysis began,  $Mn^{2+}$  was oxidized to nano-MnO<sub>2</sub> on the surface of the anode and highly dispersed in the anolyte under ultrasonic [6–8], the size of which ranged from 10 nm to 50 nm. Nano-MnO<sub>2</sub>/Mn<sup>2+</sup> presented a good reversibility with the oxidation peak and the reduction peak at 1.23 V and 1.05 V, respectively (Fig. 1). During the indirect electrosynthesis of GAD, nano-MnO<sub>2</sub>/Mn<sup>2+</sup> remained reproducible and active with negligible loss.

#### 3.2. SEM analysis of BPM

The morphology of PAM/CMC BPM was determined by scanning electron microscope (SEM, NOVA NANO SEM 230) and shown in Fig. 2. As expect, a laminate of a juxtaposed PAM layer (106  $\mu$ m thick, the anion-exchange layer, AEL) joining to CMC layer (154  $\mu$ m thick, the cation-exchange layer, CEL) with a clear interface was observed. Both layers appeared dense morphology without pores. The intermediate layer of PAM/CMC BPM was nanometer-sized (less than  $10^{-7}$  m), which meant that the electric field strength in the junction of BPM was over  $10^7$  V m<sup>-1</sup> and should lead to water splitting at 1.0 V [9].

When a potential difference was established between two electrodes, the cations migrated towards the cathode through CMC layer while the anions through PAM layer in the opposite direction. When all the salt ions initially contained were removed from the intermediate layer of BPM, the transport of electrical charge through BPM could only be accomplished by H<sup>+</sup> and OH<sup>-</sup>, and thus the water dissociation began.

Since PAM/CMC BPM possessed adequate charge densities and fine ion-exchange capacity,  $H^+$  and  $OH^-$  could be timely transferred out



Fig. 1. Cyclic voltammetry for nano- $MnO_2/Mn^{2+}$ . (Inset: TEM image of nano- $MnO_2$  in anolyte).

of the intermediate layer by  $-COO^-$  in CMC layer and  $-NR_2H^+$  in PAM layer respectively. Accordingly, the recombination of  $H^+$  and  $OH^-$  was successfully restrained. Due to the dissociation equilibrium,  $H^+$  and  $OH^-$  removed from the system would continuously be replenished. Consequently, the adequate water-dissociation resulted in a low electrical resistance and a high permselectivity of PAM/CMC BPM [10–12].

3.3. Selective electro-oxidation of glycerol by nano- $MnO_2/Mn^{2+}$  in BPM cell

Fig. 3 shows the schematic depiction of indirect electrochemical generation of GAD in PAM/CMC BPM-equipped cell using nano- $MnO_2/Mn^{2+}$  as the cyclic intermediate under ultrasonic. The electrolytic cell was divided into anode and cathode chambers by PAM/CMC BPM (effective area = 23.7 cm<sup>2</sup>). Graphite electrodes (apparent area = 5.0 cm<sup>2</sup>) were used as both cathode and anode electrodes. A mixture of MnSO<sub>4</sub> solution (0.5 mol·L<sup>-1</sup>) and glycerin was filled in the anode chamber while H<sub>2</sub>SO<sub>4</sub> solution (0.5 mol·L<sup>-1</sup>) in the cathode chamber.

When the electrolysis began,  $Mn^{2+}$  was oxidized on the surface of the anode to nano-MnO<sub>2</sub> with a larger specific surface and higher activity. Then nano-MnO<sub>2</sub> was dispersed in the anolyte under ultrasonic and selectively oxidized the primary hydroxyl groups of glycerol to GAD, while nano-MnO<sub>2</sub> itself was reversibly reduced to  $Mn^{2+}$ , and thus the cyclic oxidation–reduction reaction was carried on throughout the entire electrochemical reaction.

The main reactions of electrosynthesis of GAD were shown in Eqs. (1) and (2).

$$Mn^{2+} + 2H_2O - 2e^{-} \rightarrow MnO_2 + 4H^{+}$$
<sup>(1)</sup>

(2).

$$\begin{array}{ccc} H_{2}C - OH & HC = O \\ I \\ HC - OH + MnO_{2} + 2H^{+} \longrightarrow & \begin{array}{c} HC = O \\ I \\ HC - OH + Mn^{2+} + 2H_{2}O \\ I \\ H_{2}C - OH \end{array}$$

The whole reaction in the anode chamber was as followed:(3.



According to Eq. (3), every 1 mol GAD generated would be accompanied by the production of 2 mol  $H^+$ . Obviously, the accumulation of  $H^+$  in the anolyte was not conducive to the forward reaction. Thus, PAM/CMC BPM was applied as the separator in the electrolytic cell, which not only prevented GAD from diffusing into the cathode chamber and reversing to glycerol on the cathode, but also played an important role in the supply of  $OH^-$  to neutralize  $H^+$  accumulated during the indirect electrosynthesis of GAD.

#### 3.4. Electrosynthesis of GAD

After electrosynthesis, the anolyte was decompress-distilled until no water was left, and then an equal volume of anhydrous ethanol was added subsequently to speed up the crystallization of GAD. The final product was decompress-filtrated and dried.

As shown in Fig. 4, the sharp vibration absorption at  $2878 \text{ cm}^{-1}$ ,  $1724 \text{ cm}^{-1}$  and  $1401 \text{ cm}^{-1}$  belonged to the stretching vibration



Fig. 2. Cross-section SEM of PAM/CMC BPM.



Fig. 3. Principle of electrosynthesis of GAD by nano-MnO<sub>2</sub>/Mn<sup>2+</sup> in PAM/CMC BPM cell.

absorption of C–H, C==O and C–C in aldehyde, respectively. In brief, the electrosynthetic GAD was highly pure with the infrared spectrum similar to that of the standard GAD and the melt point ranging from 144 °C to 146 °C which accorded with the value of 145 °C in the literature [13]. After 1.5 h electrosynthesis at 75 °C and the current density of 33.3 mA cm<sup>-2</sup>, the yield of GAD approached 91.6% and the average current efficiency reached 65.5%.

#### 4. Conclusions

GAD was electrosynthesized using nano- $MnO_2/Mn^{2+}$  as the cyclic and reproducible oxidation in the electrolytic cell equipped with PAM/CMC BPM as the separator. During the indirect electrosynthesis, nano- $MnO_2/Mn^{2+}$  remained reproducible and active with negligible loss. When water dissociation occurred at the intermediate layer of BPM, OH<sup>-</sup> transferred through PAM layer and migrated into the anode room to prevent the accumulation of H<sup>+</sup> and enhance the forward reaction. The yield of GAD was 91.6% with the average current



Fig. 4. Infrared spectra of the electrosynthetic GAD and the standard GAD.

efficiency of 65.5% in PAM/CMC BPM electrolysis cell after 1.5 h electrosynthesis at 75 °C and the current density of 33.3 mA cm<sup>-2</sup>.

#### References

- [1] M.Y. Li, C.H. Zhou, J.N. Beltramini, W.H. Yu, Y.X. Fan, Prog. Chem. 20 (2008) 1474.
- [2] X.J. Wan, M.Y. Song, R. Wu, D.B. Chu, Chin, J. Appl. Chem. 20 (2003) 578.
- [3] F.W. Wang, Y.J. Wei, D.B. Chu, J. Chem. Ind. Eng. 55 (2004) 757.
- [4] F. Hanada, K. Hirayama, N. Ohmura, S. Tanaka, US 5221455, 1993.
- [5] G. Pourcelly, C. Gavach, Handbook on Bipolar Technology, Kemperman AJB, Germany, 2001.
- [6] S. Zhu, Z.Y. Zhou, D. Zhang, H.H. Wang, Microporous Mesoporous Mater. 95 (2006) 257.
- [7] V.G. Kumar, K.B. Kim, Ultrason. Sonochem. 13 (2006) 549.
- [8] L.Y. Gong, L.H. Su, H.Y. Jiang, Mater. Lett. 65 (2011) 1588.
- [9] F.G. Wilhelm, N.F.A. van der Vegt, M. Wessling, H. Strathmann, J. Electroanal. Chem. 502 (2001) 152.
- [10] C.X. Xu, R.Y. Chen, X. Zheng, X. Chen, Z. Chen, J. Membrane Sci. 307 (2008) 218.
- [11] R.Y. Chen, Z. Chen, X. Zheng, X. Chen, S.Y. Wu, J. Membrane Sci. 355 (2010) 1.
- [12] R. Simons, Electrochim, Acta, 31 (1986) 1175.
- [13] P.W. Shen, J.T. Wang, Compound Glossary, ShangHai Dictionary Press, 2002.