

# **Electrocatalytic oxidation of *n*-propanol to produce propionic acid using an electrocatalytic membrane reactor**

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## **Abstract**

An electrocatalytic membrane reactor assembled using a nano MnO<sub>2</sub> loading microporous Ti membrane as an anode and a tubular stainless steel as a cathode was used to oxidize *n*-propanol to produce propionic acid. The high efficiency and selectivity obtained is related to the synergistic effect between the reaction and separation in the reactor.

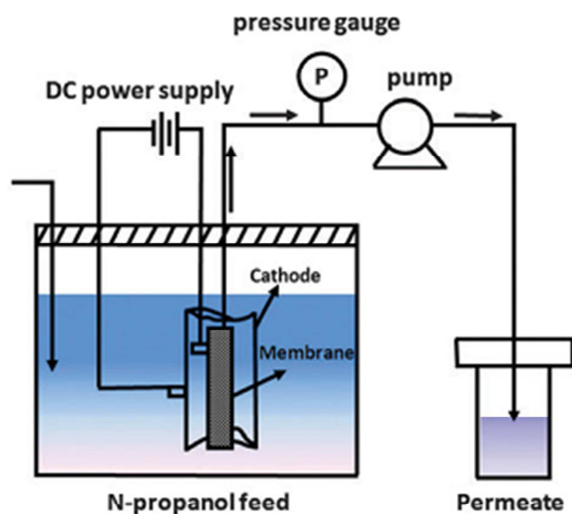
As an important chemical, propionic acid is broadly applied as food and feed preservatives, herbicides, therapeutic agents, perfumes, inhibitors, liquid crystal mixtures etc.<sup>1</sup> Industrial manufacture of propionic acid is either by chemical routes or by biological fermentation. Chemical routes include carbonylation of ethylene, oxidation of propanal and direct oxidation of hydrocarbons. However, these techniques have various disadvantages such as drastic conditions (high temperature and pressures), more than one synthetic stages and/or production of mixture that requires a further complex work-up.<sup>1</sup> Propionic acid and its salts can also be obtained by bio-synthesis with the advantage of the method being environmentally friendly and having low disposal costs. However, the severe inhibition of end-products during cell growth and the formation of by-products make its production far from satisfactory.<sup>2</sup>

With the ever-increasing need for a sustainable chemical process, tremendous attention has been paid to efficient, environmentally friendly methods for production of organic molecules.<sup>3</sup> It is noteworthy that the electrochemical method, involving electron transfer without the use of any oxidizing or reducing reagents, serves as an alternative method for the formation of useful organic compounds under mild conditions.<sup>4</sup> Nevertheless, the application of the electrochemical method in organic synthesis still remains an underdeveloped field, because the efficiency and selectivity of electrochemical reactions are limited as a result of weak cell conductivity and mass transfer on the surface of the electrode as well as the separation of reactants and products.<sup>4</sup> How to enhance the efficiency and selectivity of electrochemical reaction has become the most critical problem in the field of organic electro-chemical synthesis. A variety of new strategies such as reaction media, reaction conditions, and electrochemical devices have been employed to tackle this challenging issue.<sup>5</sup> For example, Bianchini et al.<sup>6</sup> reported selective conversion of ethanol into potassium acetate

in both passive and active direct fuel cells containing platinum-free electrodes and an anion-exchange polymer membrane. The yield of potassium acetate was 46.51%. Despite all the efforts, only a limited number of organic electrochemical processes have been developed in the industry so far.

Apart from the above-mentioned methods, the membrane-based separation and transport of the products and/or the reagents from or toward the reactor increase the yield and/or the selectivity of some processes and maximize the synergistic effects between the reaction and separation.<sup>7</sup> In addition, the membrane used to immobilize a homogeneous catalyst could realize the catalyst recovery, regeneration, and reuse in successive catalytic runs.<sup>8</sup> Recently, a simple strategy employing an electrocatalytic membrane reactor (ECMR) with a self-cleaning function has been designed for industrial wastewater purification.<sup>9</sup> A nano-TiO<sub>2</sub> loading porous conductive carbon membrane functioned both as a filter and an anode to treat oily wastewater in an ECMR. The TiO<sub>2</sub>/carbon membrane generated microflows and reactive intermediates that alleviated concentration polarization and decomposed organic foulants into CO<sub>2</sub> and H<sub>2</sub>O or small biodegradable products on the membrane surface or in pores.

To solve the challenging problem of the efficiency and selectivity in the electrochemical reaction, we propose an ECMR with a functional tubular microporous Ti membrane as both a separation barrier and an anode and a tubular stainless steel as a cathode connected by a DC regulated power supply to be used to produce propionic acid from *n*-propanol under atmospheric pressure and mild temperature (Fig. 1). In the reactor, *n*-propanol permeates the membrane from outside-in and propionic acid is obtained from the inside.



**Fig. 1** Schematic diagram of the ECMR system.

A tubular microporous Ti membrane was employed as a conductive substrate because of its significant mechanical strength, good chemical stability and specific conductivity.<sup>10</sup> Manganese dioxide was used as a catalytic layer of the electrode as it is excellent in oxidation and reduction and chemically stable.<sup>11</sup> A novel functional nano-MnO<sub>2</sub> loading porous conductive Ti membrane (MnO<sub>2</sub>/Ti) with a MnO<sub>2</sub> loading of 3.6 wt% was prepared via a sol-gel approach i.e. thermal decomposition of manganese(II) nitrate on the original titanium membrane (Experimental section in the ESI<sup>†</sup>).<sup>12</sup>

The morphology and compositions of the MnO<sub>2</sub>/Ti membrane were characterized by a HRTEM image taken from the edge of the MnO<sub>2</sub> bipyramids as shown in Fig. S1 (ESI<sup>†</sup>). The marked lattice fringes observed with an interplanar spacing of 0.31 nm are ascribed to the interplanar spacing (110) plane for the tetragonal  $\beta$ -MnO<sub>2</sub>.<sup>13</sup> Moreover, X-ray diffraction analysis and X-ray photoelectron spectroscopy revealed that the manganese oxide particles (most of  $\beta$ -MnO<sub>2</sub> and a little of Mn<sub>2</sub>O<sub>3</sub> crystallites) were well distributed on the membrane surface (Fig. S2 and S3, ESI<sup>†</sup>). With respect to oxygen transfer, MnO<sub>2</sub> is more active than

Mn<sub>2</sub>O<sub>3</sub>.<sup>14</sup> The mean diameter of MnO<sub>2</sub> crystallites was approximately 22.7 nm (Fig. S2-1, ESI†). In addition, the well-resolved lattice fringe obtained from the MnO<sub>2</sub> power represented the high crystallinity of the MnO<sub>2</sub> bipyramid, which was strongly related to the electrochemical performance of the MnO<sub>2</sub>/Ti membrane (Fig. S4, ESI†).

In the reactor,  $160 \pm 5 \text{ mmol L}^{-1}$  *n*-propanol solution (500 mL) and  $15 \text{ g L}^{-1}$  Na<sub>2</sub>SO<sub>4</sub> were used as the reactant and the aqueous electrolyte, respectively. The ECMR was operated in the dead-end mode and the operating voltage was 2.8 V, which was the optimum value (Table S1, ESI†). A suction pump (BT100-2J) was used to control the residence time (RT). The residence time (min) was defined as the ratio of the volume of the membrane pore (cm<sup>3</sup>) to the flow rate of solution (mL min<sup>-1</sup>).<sup>15</sup>

In general, oxidation of *n*-propanol leads to the production of propanal and propionic acid (Fig. S5 and Table S2 in the ESI†), which were determined using GC.<sup>16</sup> Changes in the concentration of feed and permeate compositions with RT from 0 min to 22.55 min are illustrated in Fig. 2.

As shown in Fig. 2a, when the residence time was 0 min, namely the ECMR is similar to a conventional electrocatalytic reactor without any permeation, the concentration of *n*-propanol in the membrane reactor decreased from 157 to 143 mmol L<sup>-1</sup>, and the concentration of propanal and propionic acid increased from 0 to 0.13 mmol L<sup>-1</sup> and 0.26 mmol L<sup>-1</sup>, respectively, during the 75 min operation at 25 °C. Thus, the corresponding conversion and selectivity in the conventional electrocatalytic reactor were very low, approximately 7% and 5%, respectively (Fig. S6, ESI†). The reason was that the initial electrocatalytic oxidation of

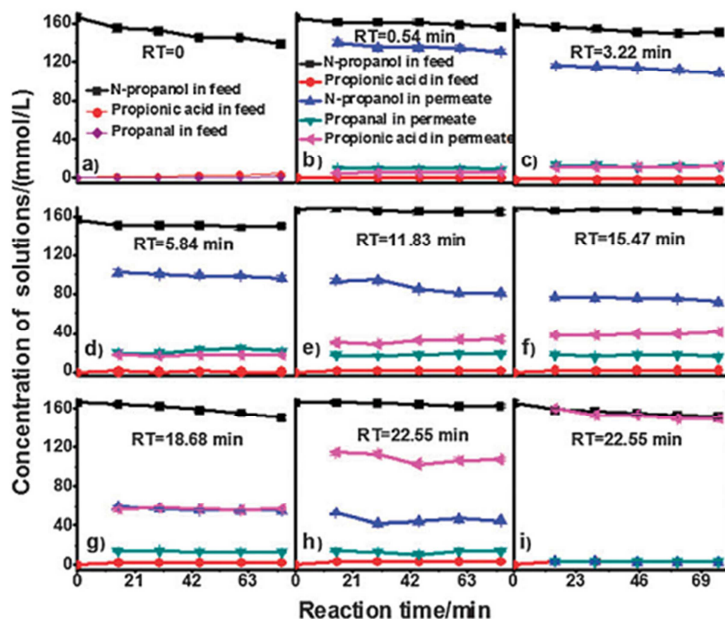
*n*-propanol on the surface of the membrane electrode constrained the diffusion in the reactor, thereby preventing a new oxidation reaction.<sup>17</sup>

Further, the concentration of *n*-propanol in the reactor decreased slightly from 165 to 156 mmol L<sup>-1</sup> at 0.54 min of the residence time and the concentration of propionic acid was kept at about 0.01 mmol L<sup>-1</sup> (Fig. 2b). It implied that the concentration of the reactant – *n*-propanol was maintained at a high level and the concentration of the product – propionic acid – was quite low during the ECMR operation. In the permeate, the concentration of *n*-propanol was 135.66 mmol L<sup>-1</sup>, and about 9.30 mmol L<sup>-1</sup> propanal and 6.50 mmol L<sup>-1</sup> propionic acid were produced by the oxidation of *n*-propanol, respectively.

Upon further increasing the residence time from 3.22 to 22.55 min at 25 °C, the concentration of *n*-propanol in the reactor remained quite stable in the range of 167.29 to 150.91 mmol L<sup>-1</sup> (Fig. 2c–h), and only traces of propionic acid (0–2.64 mmol L<sup>-1</sup>) were detected. It suggested that the produced propionic acid might flow through the membrane into the permeate. In the permeate, the concentration of *n*-propanol dropped from 114.32 to 42.99 mmol L<sup>-1</sup>, whereas the concentration of propionic acid increased from 12.94 to 104.09 mmol L<sup>-1</sup>. Besides, an interesting phenomenon was that only a small amount of propanal in the range of 12.55–22.71 mmol L<sup>-1</sup> remained in the permeate.

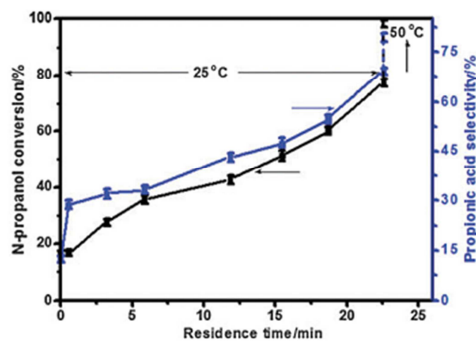
When the reaction temperature increased from 25 to 50 °C at a residence time of 22.55 min, the concentration of propionic acid in the permeate increased from 104.09 to 152.5 mmol L<sup>-1</sup>, while the concentration of *n*-propanol decreased from 42.99 to 2.59 mmol L<sup>-1</sup> (Fig. 2i). In the meantime, it was found from the carbon molar mass balance before and after the electrocatalytic reaction that only a little amount of *n*-propanol (0.85–21.83 mmol) might be

completely mineralized into CO<sub>2</sub> and H<sub>2</sub>O or reacted with the generated acid to produce propyl propionate by esterification during the ECMR operation (Table S3, ESI†).



**Fig. 2** Concentration of feed and permeate compositions *versus* reaction time at different residence times and temperatures (a–h: the reaction temperature at 25 °C; i: 50 °C).

Changes in the conversion of *n*-propanol and selectivity to propionic acid versus residence time and reaction temperature in the ECMR are plotted in Fig. 3. 60.77% and 56.82% improvements in the *n*-propanol conversion (from 16.46% to 77.23%) and the selectivity to propionic acid (from 12.42% to 69.24%) were achieved with an increase in the residence time from 0 min to 22.55 min, respectively. The results also confirmed that the longer residence time the reaction was carried out for in the ECMR, the more amount of *n*-propanol was oxidized to propionic acid (Fig. 2b–h).



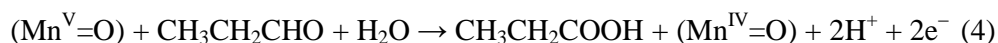
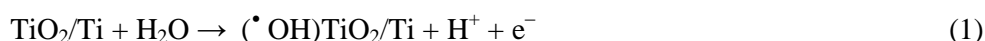
**Fig. 3** Conversion of *n*-propanol and selectivity to propionic acid *versus* residence time and reaction temperature.

With the reaction temperature rising from 25 to 50 °C, the conversion of *n*-propanol and the selectivity to propionic acid reached the highest value of 98.44% and 79.33%, respectively. It revealed that a higher reaction temperature could promote the collision of the reactants, thereby enhancing the reaction rate.<sup>18</sup> Therefore, the results revealed that the residence time and reaction temperature play the key role in the oxidation process of *n*-propanol as well as the production of propionic acid in the ECMR. Besides, the production efficiency of propionic acid is governed by the synergistic effect between membrane separation and electrocatalytic oxidation in the ECMR.<sup>9</sup>

Since the selection of electrode material was essential to electro-catalytic oxidation processes, oxide electrodes are likely to be suitable for carbohydrate oxidation because these molecules are expected to get adsorbed on the oxide layer easily through formation of hydrogen bonds *via* the OH groups, and facilitate electron transfer. Thus, MnO<sub>2</sub> can be considered a good electrocatalyst owing to the fact that it possesses a number of higher valent oxo-manganese species such as Mn(IV) and Mn(V), which are generally strong chemical oxidants.<sup>19</sup> During the ECMR operation, the TiO<sub>2</sub> catalyst formed during the preparation processes of Ti and MnO<sub>2</sub>/Ti membranes (Fig. S2 and S3, ESI†) was electrified to generate



the electron–hole pair, which interacted with H<sub>2</sub>O to produce absorbed hydroxyl radicals on the membrane surface [eqn (1)].<sup>20</sup> Then the absorbed hydroxyl radicals interacted with the oxygen of the MnO<sub>2</sub> lattice in the MnO<sub>2</sub>/Ti anode to generate a higher valent oxo-manganese species (Mn<sup>V</sup>=O) oxide [eqn (2)].<sup>21</sup> As a strong chemical oxidant, the higher valent oxo-manganese species reacted with the absorbed *n*-propanol molecule to produce propanal or propionic acid by a redox reaction or electron transfer [eqn. (3 and 4)].<sup>22</sup> At the same time, the higher valent oxo-manganese species could be consumed chemically by organics and reduced to MnO<sub>2</sub> (Mn<sup>IV</sup>=O), which continuously interacts with the absorbed hydroxyl radicals to form a higher valent oxo-manganese species.<sup>21</sup>



Based on the above discussion, a possible reaction pathway for *n*-propanol electrochemical oxidation using the MnO<sub>2</sub>/Ti membrane was proposed (Fig. S7, ESI<sup>†</sup>). Here Mn=O represents a pair of adjacent Mn and O atoms at the surface of the MnO<sub>2</sub> matrix. Electrocatalysis takes place by successive generation and consumption of a Mn(V) species (Fig. S8, ESI<sup>†</sup>).

Normally, an electrocatalytic membrane reactor is a piece of chemical equipment that combines a catalyst-filled reaction chamber with a membrane in order to add reactants or remove products or by-products of the reaction. In ECMR operation, the final product propionic acid and low concentration of the intermediate product propanal were removed through the membrane in the reaction zone so as to enhance the conversion and selectivity

due to the forced across flow-mode.<sup>7</sup> The maximum filtration rate was 5.00 ml min<sup>-1</sup> at a residence time of 0.54 min (Table S4, ESI†). Meanwhile, as the larger surface area of the MnO<sub>2</sub>/Ti membrane (230 m<sup>2</sup> g<sup>-1</sup>) could intensify the contact between reactants and catalyst, the forced convection and diffusion promoted the *n*-propanol molecule to transport to the surface of the MnO<sub>2</sub> catalyst during the ECMR operation.<sup>7</sup> As a result, the synergy between electrocatalytic oxidation and membrane separation led to the high effectivity and selectivity of propionic acid production from *n*-propanol.

In conclusion, a novel functional nano-MnO<sub>2</sub> loading porous Ti membrane was prepared and employed as the anode to produce propionic acid from *n*-propanol in an ECMR. Propionic acid could be produced effectively by electrocatalytic oxidization of *n*-propanol by controlling the residence time and reaction temperature. Such an ECMR described here would have a wide range of potential applications in the field of electrochemical organic synthesis.

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