



An electrocatalytic reactor for the high selectivity production of sodium 2,2,3,3-tetrafluoropropionate from 2,2,3,3-tetrafluoro-1-propanol



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ABSTRACT

In order to realize green and highly selective oxidation of 2,2,3,3-tetrafluoro-1-propanol (TFP) into high value-added chemicals-sodium 2,2,3,3-tetrafluoropropionate (STFP), a functional electrocatalytic reactor (ECR) with nano-MnO_x loading porous Ti electrode as anode was used for the oxidation of TFP to produce 2,2,3,3-tetrafluoropropionic acid (TFPA), which reacted with the electrolyte-NaOH to yield STFP. During the ECR operation, the effects of operation parameters such as pH value of the feed, residence time (RT), reaction temperature, current density and TFP concentration on TFP conversion and selectivity to STFP were investigated. Response Surface Methodology (RSM) was employed to further optimize the effect and interaction of different operation parameters on TFP conversion according to the single factor experiment results. It is found that the interaction of RT and reaction temperature was the most significant. The conversion of TFP reached to 91.9% with a selectivity to STFP over 99.9% under the optimum conditions of reaction temperature 80 °C, RT 25 min, TFP concentration 26.3 mmol L⁻¹ and current density 3.4 mA cm⁻². The high performance obtained is associated with the synergistic effect between electrochemical oxidation and convection-enhanced diffusion in the ECR.

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1. Introduction

Sodium 2,2,3,3-tetrafluoropropionate (STFP) has, over recent years, increasingly attracted attention as a new pesticide for weed-icide due to its low toxicity, high efficiency, high selectivity and environmental friendliness [1–3]. It is also an important chemical intermediate for the preparation of cleaning agents [1]. The current industrial synthesis methods of STFP are mainly based on conventional organic syntheses, including nucleophilic addition of tetrafluoroethylene, telomerization of tetrafluoroethylene and oxidation of 2,2,3,3-tetrafluoro-1-propanol (TFP) [2–5]. For example, Krespan et al. reported that tetrafluoroethylene reacted with sodium cyanide and water to yield STFP in the presence of methanol at the reaction temperature of 100 °C and the pressure of 598–791 kPa. Although the conversion of product obtained was as high as 83%, this method has been forbidden owing to the high toxicity of sodium cyanide [2,3]. Hence, it is of great practical importance to develop an environmentally friendly process to produce STFP from TFP.

Geng et al. investigated telomerization of tetrafluoroethylene to produce TFP in the presence of methanol, and with the high cost of STFP production was obtained by oxidation of TFP with potassium permanganate in sodium hydroxide solution [4]. In addition, Xiao et al. presented a method to produce 2,2,3,3-tetrafluoropropionic acid (TFPA) by oxidation of TFP with hydrogen peroxide at the reaction temperature of 120 °C and the pressure of –90 kPa. Then, TFPA reacted with the sodium hydroxide to prepare STFP at pH 7–8. The conversion of TFP and the selectivity to STFP reached to 59.1% and 79.8%, respectively [5]. These synthesis routes, however, have various disadvantages, such as rigorous conditions, formation of by-products and more than one synthetic stages and/or production of mixture that requires a further complex posttreatment [2–5], which make their production and cost far from satisfactory. Thus, a major challenge is to develop a green and highly efficient route to produce STFP.

With the ever-increasing need for green and sustainable chemical processes [6], the electrochemical method, involving the transfer of electrons without the use of any oxidizing or reducing reagents, is promising to serve as an alternative method for the formation of useful organic compounds under mild conditions [7,8]. Nevertheless, the application of the electrochemical method in organic synthesis still remains an underdeveloped field,

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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 [7]. Thus, how to enhance the efficiency and selectivity of the electrochemical reaction has become the most critical problem in the field of organic electrochemical synthesis. To tackle this issue, various new strategies have been carried out, such as using large surface area electrodes, modification of electrodes, moving electrodes to offer larger mass-transport parameters and adding mediators that act as electron carriers between the electrode and the substrate [9,10]. Despite all the efforts, only a limited number of organic electrochemical processes have been developed in the industry so far.

Recently, to tackle the challenging problem of the efficiency and selectivity in electrochemical reaction, a design of electrocatalytic reactor (ECR) with reaction and convection-enhanced diffusion function has been designed for the electrocatalytic oxidation of n-propanol to produce propionic acid in our previous work [11]. An ECR assembled by a nano-MnO_x loading porous titanium (Ti) electrode (MnO_x/Ti) as an anode and a stainless steel as a cathode was used to oxidize n-propanol to produce propionic acid under atmospheric pressure and mild temperature. Here a tubular porous Ti electrode was employed as a conductive substrate because of its significant mechanical strength, good chemical stability and specific conductivity [11]. MnO_x could be considered as a good electrocatalyst owing to the fact that it possesses a number of higher valent oxo-manganese species such as Mn^{IV}=O, which are generally used as strong chemical oxidants [12]. Repeated switching between two such species at the anode is expected to lead to the oxidation of alcohols [12,13]. During the ECR operation, n-propanol permeated the electrode from outside-in and propionic acid was obtained from the inside. Propionic acid could be produced effectively from electrocatalytic oxidation of n-propanol by controlling the residence time and reaction temperature. The conversion of n-propanol reached to 98.44%, and the selectivity to propionic acid was 79.33% under the operation conditions of reaction temperature 50 °C, residence time 25 min, n-propanol concentration 160 mmol L⁻¹ and operation voltage 2.8 V. The high efficiency of the ECR is attributed to the synergetic effect of reaction and convection-enhanced diffusion.

In addition, a number of factors including pH value of the feed, residence time, reaction temperature, current density and reactants concentration would influence the efficiency of reaction during the ECR operation [11,14]. Recently, Response Surface Methodology (RSM) has been employed to optimize and understand the performance of complex systems [15–17]. By the application of RSM, it is possible to evaluate the interactions of possible influencing factors on reaction efficiency with a limited number of planned experiments.

In order to realize green and highly selective oxidation of TFP into high value-added chemicals—STFP, the aim of the present study is to design a functional ECR with nano-MnO_x loading porous Ti electrode as anode for the oxidation of TFP to produce TFPA under mild conditions, which reacted with the electrolyte-NaOH to yield STFP. Meanwhile, RSM with trial version of Design Expert 7.1.3 was applied for the optimization of the operation parameters of ECR during the electrocatalytic oxidation of TFP to produce STFP.

2. Experimental

2.1. Materials

Commercially available tubular porous Ti electrode was purchased from Shanghai Yiming Filtration Technology Co., Ltd. China. The electrode has an average pore size of 7.0 μm, 30 mm in outer diameter, 20 mm in inner diameter, and an electrode geometric

surface area of 37.7 cm². The reference samples of TFP and STFP were of chromatographic pure and purchased from Merger CO., Ltd. All other reagents were of analytical grade and purchased from Kermel (Tianjin Kermel chemical reagent Co., Ltd, China) and used as received without further purification.

2.2. Preparation and characterization of MnO_x/Ti electrode

A novel functional nano-MnO_x loading tubular porous Ti electrode (MnO_x/Ti electrode) was prepared via a sol-gel approach i.e. thermal decomposition of manganese (II) nitrate on the original tubular porous Ti electrode [11]. The procedure is briefly described as follows: a commercially available tubular porous Ti electrode with an electrode volume of 15.7 cm³ was used as a substrate. The electrode was first pretreated in 10 wt% boiled oxalic acid solution for 1 h, cleaned with large amounts of deionized water and dried at room temperature. The electrode was then dipped into 50 wt% Mn(NO₃)₂ solution for 0.5 h. After removing from the solution, it was dried at room temperature. The treated electrode was placed in a muffle furnace to sinter at a designed temperature for 2 h, then cooled to room temperature naturally. A functional nano-MnO_x loading tubular porous Ti electrode (porous MnO_x/Ti electrode) was finally obtained.

The morphology and pore structure of MnO_x/Ti electrode was observed by field-emission scanning electron microscopy (FESEM) (Hitachi S-4800), high-resolution transmission electron microscopy (HRTEM) (JEM-2100). The chemical composition of MnO_x/Ti electrode was evaluated by energy dispersive spectrum (EDS) and X-ray diffraction (XRD) patterns. XRD patterns were obtained using Bruker AXS D8 Advance (Germany) with Cu Kα λ = 1.5406 Å. The scanning rate was 2°/min in 2θ mode from 20° to 80°.

2.3. Electrochemical measurements

The electrochemical measurements were conducted on an electrochemical workstation (Zahner-Zennium) instrument in a three-electrode cell at room temperature. A saturated calomel electrode (SCE) for alkaline solutions was used as the reference electrode, a platinum foil was used as the counter electrode, and a original Ti electrode or MnO_x/Ti electrode was used as working electrode for the test. All the potentials were given with respect to a reference hydrogen electrode (RHE). The electrochemical activities of original Ti electrode and MnO_x/Ti electrode were evaluated through electrochemical impedance spectroscopy (EIS) with an amplitude of ± 10 mV in the frequency range of 10 mHz to 1 MHz in 0.1 M NaOH solution. All solutions were prepared using deionized water.

2.4. Electrocatalytic reactor

The schematic diagram of electrocatalytic reactor (ECR) system was showed in the Fig. 1. The MnO_x/Ti electrode was arranged in the center of the feed tank. The distance between anode and cathode was 40 mm. In the reactor, the MnO_x/Ti electrode as the anode and the stainless steel tube surrounding the electrode as the cathode were connected by a direct current (DC) regulated power supply (Maynuo Electronics M8811) to constitute the ECR. The bottom of the tubular MnO_x/Ti electrode was closed with a disc. A peristaltic pump (Longer Pump BT100-2J) was used to suck the filtrate through the electrode from feed tank to permeate tank in a dead-end manner as well as to control residence time of the ECR (5–25 min). The electrocatalytic oxidation of TFP was carried out with ECR under atmospheric pressure. The pH value of the feed (pH 9.0–13.0) was controlled by adding NaOH. At the same time, the similar ionic strength of the solution was controlled by adding

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