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Efficiently electrochemical removal of nitrite contamination with stable RuO_2-TiO_2/Ti electrodes

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ABSTRACT

RuO_2-TiO_2/Ti electrode was prepared for the electrocatalytic removal of nitrite in this work. The influences of calcination temperatures on crystal phase and morphology of RuO_2-TiO_2 composite were explored by XRD and TEM. The formation of RuO_2 epitaxial layers on the surface of TiO_2 by calcination at 400 °C reduces the impedance (EIS test) and improves the electrocatalytic activity for RuO_2-TiO_2. The CV test shows that the electrochemically surface active sites increase along with the increase of RuO_2 content from 0 to 2.0 wt%. The nitrite removal rate of 2.0 wt% RuO_2-TiO_2/Ti electrode is found ca. 6.7 and 2.5 times faster than those of 0.02 wt% and 0.1 wt% RuO_2-TiO_2/Ti electrodes, respectively. Oxidation of the active sites on the RuO_2 results in an obvious activity decrease for RuO_2/Ti and RuO_2-TiO_2/Ti electrodes in just 3 reaction cycles (30 min/cycle). By exchanging the anode and cathode after every cycle, the catalytic activity of corresponding 2.0 wt% RuO_2-TiO_2/Ti electrode remains almost unchanged after 50 cycles. Although the electrocatalytic service life of RuO_2/Ti electrode is also greatly improved, its electrocatalytic activity decreases much after 50 cycles. The relatively longer service life of 2.0 wt% RuO_2-TiO_2/Ti electrode should own to the intensified interaction between the epitaxially spread RuO_2 and TiO_2, which stabilizes the chemical states of RuO_2. The main product for the electrocatalytic removal of nitrite is nitrate by indirect oxidation, while a small amount of ammonium is also produced at the cathode. The as-produced ammonium will be oxidized into nitrogen molecule, which is released from the aqueous solution afterwards and contributes the decrease of the total content of N in the solution.

1. Introduction

Nitrite (NO_2^-) contamination in water resources has received particularly environmental concerns, as it causes serious human health problems like liver damage, blue baby syndrome and cancers [1,2]. To safeguard people's health, the concentration of NO_2^- over 0.5 mg L^{-1} in drinking water is not allowed [3]. Many conventional treatments, such as physical-chemical adsorption with activated carbon [4], biological processes [5], and chemical oxidation with oxidants [6] are adopted to remove nitrite from the water. However, high costs, secondary pollution, low running efficiency, and other disadvantages prevent them from applying effectively in many cases [4–7]. To avoid these shortages, electrochemical catalysis is recommended as an environmental-friendly progress. Generally, it can be easily operated, feasible to be automated process, and low cost. Nowadays, electrochemistry method is increasingly applied in the wastewater treatment. Electrochemical oxidation can effectively oxidize nitrite ion [8] and organic pollutants in aqueous solution by direct or indirect oxidation [9]. Several electrode materials, such as SnO_2/Ti [10], RuO_2/Ti [11], IrO_2/Ti [12] and boron-doped diamond [13], have been used for the electrolytic treatment processes, of which the electrodes are composed of transition metal oxides. The M_1O_x-M_2O_x/Ti electrodes used in these cases are called dimensionally stable anodes (DSA), which gives more advanced performances (catalytic activity, stability and low cost) than those of conventional anodes (metal, carbon, etc) [14–17]. Generally, indirectly electrochemical oxidation [18] is suggested as the main process that occurs in the electrolytic wastewater treatment, in which an anodic electrocatalysis leads to the generation of hydroxyl radicals ($OH^•$) or active chlorine species (ClO^-) in the presence of chloride ion [19]. Specifically, most of DSA electrodes (SnO_2-Sb/Ti [20], PbO_2/Ti [21]) tend to produce $OH^•$ to oxidized pollutants, while RuO_2-TiO_2/Ti electrode and IrO_2-TiO_2/Ti [22] are prone to produce ClO^-.

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Based on the isomorphism rule, ions of the same type with similar ionic radius can co-exist in the same lattice. Accordingly, the ionic radius of Ru^{4+} and Ti^{4+} are 0.065 nm and 0.064 nm, respectively; therefore, RuO_2 and TiO_2 could form a solid solution and give strong junction at their interface [23], which brings the RuO_2-TiO_2/Ti electrode excellent electric conductivity. Consequently, RuO_2-TiO_2/Ti electrode is effectively applied in the chlor-alkali processes for its low chlorine evolution potential, relatively high oxygen evolution potential and excellent electric conductivity [24,25]. However, the further applications of the RuO_2-TiO_2/Ti electrode are limited by the short service life in anodic polarization conditions and the occurrence of the coating shedding [23,24,26]. Our work aims to evaluate the electrocatalytic performance and the electrochemical stability of RuO_2-TiO_2/Ti electrode during the nitrite removal process, as well as the relationship between chemical state and electrochemical activities of RuO_2-TiO_2 composite. In addition, the electrochemical nitrite-N removal mechanism is suggested according to the experimental observations.

2. Experimental section

2.1. Reagents and materials

TiO_2 (P25, Evonik Degussa), $RuCl_3$ (AR) were obtained from commercial sources. NaCl, $NaNO_2$, KNO_3, Na_2SO_4 and NH_4Cl were obtained from Sinopharm Chemical Reagent. All the reagents were AR and used as received. Ultrapure water (18.2 MΩ) was used throughout the work.

2.2. Preparation of RuO_2-TiO_2/Ti electrode

2.2.1. Synthesis of RuO_2-TiO_2 composite

A hydrothermal method was used to prepare RuO_2-TiO_2 composite just as our previous report [27]. A desired amount of $RuCl_3$ was mixed with the specified amount of TiO_2 in different ratios (0 wt%, 0.02 wt%, 0.1 wt%, 2.0 wt%, 100 wt%) using water as the solvent to ensure a total volume of 75 mL. Then the mixture was transferred into a 100 mL autoclave and heated at 180 °C for 10 h. After cooling down, the product was separated by centrifuging, washed with water for three times, and dried at 60 °C under vacuum overnight to get the RuO_2-TiO_2 catalysts.

2.2.2. Electrode preparation

The electrode was prepared from titanium plate with 0.50 mm thickness. The titanium plate (4.0 cm × 7.5 cm) was first degreased in 0.50 M NaOH aqueous solution at 60 °C for 30 min, then washed with water and sonicated in ethanol for 30 min. Next, it was polished with 1000-mesh emery paper and etched in 10 wt% boiling oxalic acid solution for 2.5 h [23]. Then, the titanium plate was washed with water, sonicated for 15 min, and dried for use.

The painting suspension was prepared by dispersing the above-prepared RuO_2-TiO_2 composite in ethanol under ultrasonic condition. Then the prepared painting suspension was pasted to the pretreated titanium plates (4.0 cm × 7.5 cm) with a brush. The painted Ti plate was then dried at 100 °C for 10 min. In the same way, the other side of the titanium plate was also coated. The coating process was repeated for several times to load a desired amount of catalysts. The total mass of the deposited composite was fixed to 0.04 g for each side. Finally, the plate was calcined under the desired temperature (200 °C, 300 °C, 400 °C, 500 °C, and 600 °C) for 10 h to obtain a RuO_2-TiO_2/Ti active electrode.

2.3. Catalyst characterization

The crystalline structure of RuO_2-TiO_2 catalysts was measured by X-ray diffraction (XRD). Diffraction patterns of the samples were performed using an X-Ray diffractometer (Rigaku Ultima IV) operating in the reflection mode with Cu Kα radiation. A continuous scan mode was employed to collect 2θ data from 10° to 80° with a scan step of 0.02°. Transmission electron microscopy (TEM) was investigated using a JEOL JEM 2100F instrument operated at 200 kV. The morphologies of the samples were pictured with SEM (Tescan VEGA 3 SBU) observation. The chemical compositions of samples were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Fisher ESCALAB 250Xi system with Al Kα radiation), and calibrated internally by carbon deposit C1s binding energy (BE) at 284.6 eV.

2.4. Electrochemical measurements

The electrochemical properties of RuO_2-TiO_2 electrodes were analyzed through cyclic voltammetry (CV), polarization tests and electrochemical impedance spectroscopy (EIS). The electrochemical measurements were carried out in a three-electrode system (electrochemical workstation, Zahner Co., Germany) with a Pt electrode as the counter electrode, a Saturated Calomel Electrode (SCE) as the reference electrode, and RuO_2-TiO_2/Ti electrode as the working electrode. The effective working area of the electrode was 4.0 cm × 5.5 cm. The electrolytes for polarization tests were 0.05 M NaCl (for chlorine evolution potential test) and 0.0167 M Na_2SO_4 aqueous solution (for oxygen evolution potential test). The CV tests were carried out in 0.05 M NaCl and 10 ppm $NaNO_2$ aqueous solution. Cyclic voltammograms were recorded between −3.0 and 3.0 V_{SCE} at a scan rate of 100 mV s^{-1}. The EIS spectra of electrode materials were analyzed by using 2.5 mM $K_3Fe(CN)_6$/$K_4Fe(CN)_6$ (1:1) and 1.0 M KCl aqueous solution as the electrolyte. The frequency ranged from 0.01 Hz to 10 MHz and the amplitude of the potential was 3.0 V. The measured EIS data were analyzed and fitted to the equivalent electrical circuits by ZSimpWin software.

2.5. Electrocatalytic removal of nitrite

A DC potentiostat (APS3005DM, ATTEN instrument, China) was employed as the power supply for electrochemical reactions. Synthetic nitrite solution at a concentration of 10 mg L^{-1} $NaNO_2$ was used. The volume of each solution with 0.05 M NaCl for electrochemical test was 250 mL. The RuO_2-TiO_2/Ti electrodes were used as both the anode and cathode, which were placed vertically in parallel in the reactor with a gap of 1.0 cm. The immersed areas of the anodes and cathodes in the treated solution were both 4.0 cm × 5.5 cm. The applied voltage was fixed at 5.0 V. Unless specially stated, all the tests were carried out at room temperature (25 °C).

2.6. Analysis of aqueous N-species

Generally, the main aqueous soluble N-products in this work are nitrate, nitrite and ammonia. Nitrate-N and ammonia-N were measured by an ionometer (PXS-270, Shanghai INESA Scientific Instrument) with ion selectivity electrodes (PNO_3-1-01, PNH_3-1-01, Shanghai INESA Scientific Instrument), whereas nitrite-N was analyzed with a colorimetric method on an ultraviolet-visible spectrophotometer (UV-2600, Shimadzu). According to the fact that the NO_2^- forms red dye when coupling with sulfanilamide, the NO_2^- concentration can be analyzed by measuring the absorbance of red dye at the wavelength of 540 nm [28]. Briefly, 2.5 mL sample solution and 1 mL sulfanilamide were added into a 50 mL volumetric flask. Then the solution was adjusted to pH 1.8 by phosphoric acid, and diluted with water to a volume of 50 mL. After 30 min, the as-prepared red solution was analyzed by recording variations of the absorbance at 540 nm with a UV-2600.