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Use of a vanadium nanostructured material for hydrogen peroxide electrogeneration

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ABSTRACT

This paper reports the use of different proportions of vanadium nanostructured electrocatalysts for H_2O_2 electrogeneration. A comparative study using different mass proportions of vanadium (1%, 6%, 12%, 15% and 20%) was performed to produce H_2O_2. The V/C materials were prepared by a modified polymeric precursor method (PPM) and characterized by X-ray diffraction and transmission electron microscopy (TEM) analysis. XRD results identified different phases comprising V_2O_5 and VO_2 while TEM micrographs show the vanadium nanoparticles in the range of 1–3 nm. The rotating ring–disk electrode (RRDE) technique was used to evaluate the kinetics of the oxygen reduction reaction (ORR). The results showed that the 12% V/C prepared by the PPM was the best composite among those investigated for the production of H_2O_2 in a 1 mol L^{-1} NaOH electrolyte solution because this electrocatalyst exhibited a H_2O_2 conversion efficiency of 68%. The ring current obtained with 12% V/C was greater than the obtained with Vulcan carbon, which was used as a reference material for H_2O_2 production and exhibited an efficiency of 31%. After the study with the RRDE, gas-diffusion electrodes (GDEs) containing the catalyst were used to evaluate the amount of H_2O_2 produced during exhaustive electrolysis. On the basis of these results, the 12% V/C GDE produced 620 mg L^{-1} of H_2O_2 in alkaline media, whereas the Vulcan carbon GDE produced only 369 mg L^{-1} at the same potential. In acidic media, the 12% V/C GDE produced 107 mg L^{-1} of H_2O_2, whereas Vulcan carbon produced only 72 mg L^{-1} at the same potential, indicating the better activity of V/C for H_2O_2 electrogeneration. The 12% V/C is composed primarily of the V_2O_5 phase, which shows acidic character that can increase the acidity of the surface, providing greater hydrophilicity and, consequently, greater activity toward the ORR via two-electron transference.

1. Introduction

Increasing demand and shortage of clean water sources due to rapid industrialization, population growth and long-term droughts have become an issue worldwide. One of the most pervasive problems affecting people throughout the world is inadequate access to clean water and sanitation [1,2].

Approximately 4 billion people worldwide have no or little access to clean and sanitized water, and millions of people die of severe waterborne diseases annually [1,2]. These statistics are expected to increase with the increasing of water contamination due to the excessive discharge of pollutants and contaminants into the natural water cycle [1–3]. In view of the need for clean water, more effective and lower-cost technologies for wastewater treatment are desirable.

Currently available water treatment technologies, such as adsorption by activated carbon and air stripping, merely concentrate the chemicals present by transferring them to the adsorbent or air; they do not convert them into non-toxic wastes [4]. Consequently, the development of newer eco-friendly methods of destroying pollutants found in wastewater has become an imperative task and, ultimately, the objective of research centered on advanced oxidation processes (AOPs) [5].

AOPs rely on the *in situ* generation of highly reactive radical species, mainly hydroxyl radicals, which are able to oxidize and mineralize almost any organic molecule, yielding CO_2 and inorganic ions. AOPs are also characterized by their non-selective attack, which is a useful attribute for wastewater treatment and a potential solution to pollution problems [2,5].

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Considering the AOPs, hydroxyl radicals can be generated by different routes using various processes such as ozonation, ozone in combination with UV irradiation (O_3/UV), ozone and hydrogen peroxide (O_3/H_2O_2), hydrogen peroxide and ultraviolet light (UV/H_2O_2) and Fenton's reagent (Fe(II)/H_2O_2) in combination with the photo-Fenton reaction (UV/Fe(II)/H_2O_2) [6–11]. All these processes involve the generation of hydroxyl radicals ($^{\cdot}OH$), which have an oxidation potential (2.8 V) greater than that of hydrogen peroxide (1.8 V) and ozone (2.1 V) and are able to oxidize almost any organic pollutant [12,13].

Among the various approaches to generating hydroxyl radicals, the Fenton reaction has attracted substantial attention due to its low environmental impact; it is one of the cleanest and most efficient processes for eliminating toxic compounds in wastewaters [13,14]. Iron is a highly abundant and non-toxic element, and hydrogen peroxide breaks down to environmentally benign products [14].

In view of producing hydroxyl radical by hydrogen peroxide it could be generated by the ORR via the two-electron pathway, and carbon electrodes are the reference material for H_2O_2 production via the ORR in alkaline media [15–17]. Moreover, the addition of metal oxides onto carbon electrodes to enhance their activity and promote the two-electron transfer during the ORR has already been described [18–20].

Considering the use of metal oxides for hydrogen peroxide production, vanadium is one of the most abundant and widely distributed metals in the earth's crust [21] and serves as an important catalyst in both chemical and biochemical systems. The utility of vanadium as a catalyst stems from its facile inter-conversion among the higher oxidation states of vanadium and its ability to activate molecular oxygen [22].

In order to improve the hydrogen peroxide electrogeneration, this work investigates five compositions of vanadium oxide nanoparticles supported on Vulcan carbon (1%, 6%, 12%, 15% and 20% V/C) as electrocatalysts for the production of H_2O_2 via the ORR. After identified the best composition of vanadium electrocatalyst, gas diffusion electrodes were confectioned to quantify the H_2O_2 production. Vanadium dissolution was also evaluated in different media using graphite-furnace atomic absorption spectrometry (GF AAS).

2. Materials and methods

2.1. Vanadium electrocatalyst preparation

Vanadium oxide nanostructured materials at 1%, 6%, 12%, 15% and 20% (w/w) on Vulcan XC 72R carbon were prepared using the PPM, as described by De Souza et al. [23–26]. The precursor solution was prepared by dissolving citric acid into ethylene glycol at a 50:400 ratio at 60 °C. Afterward, vanadium chloride, VCl_3 (Sigma–Aldrich®), was added to this first solution in different amounts, maintaining a ratio of 1:50:400 (metal:citric acid:ethylene glycol), producing a viscous resin. Subsequently, an appropriate amount of Vulcan XC-72R carbon (Cabot Corporation) was added to the resin formed initially to obtain the electrocatalysts with different compositions. The mixtures were homogenized in an ultrasonic bath for 60 min and then thermally treated at 400 °C for 2 h under an N_2 atmosphere.

2.2. Characterization of vanadium nanomaterials

2.2.1. X-ray diffraction, transmission electron microscopy and energy-dispersive spectrometry analysis

The vanadium oxide electrocatalysts were characterized by X-ray diffraction (XRD) using a D8 Focus diffratometer (Bruker AXS) equipped with a Cu Kα radiation source operated in the continuous scan mode (2° min^{-1}) from 20 to 80°. TEM images were also carried out using a JEOL transmission electron microscope model JEM-2100 operated at 200 kV.

The 12% V/C was also characterized by energy-dispersive spectrometry analysis (EDS) using an LINK ANALYTICAL EDX unit (Isis System Series 200) with a SiLi Pentafet detector and an ultrathin ATW II (Atmosphere Thin Window); the resolution range was 133 eV–5.9 keV. The instrument was coupled to ZEISS LEO 440 electronic microscope (Cambridge, England). For calibration, a Co standard was employed; an electron beam of 20 kV, a focal length of 25 nm, a dead time of 30%, a current of 2.82 A and an I probe of 950 pA were used.

2.2.2. Electrochemical characterization

Electrochemical characterizations were performed using the rotating ring–disk technique with an Autolab PGSTAT 302N potentiostat/galvanostat. For these measurements, a platinum wire, Hg/HgO and a rotating ring–disk electrode (Au–glassy carbon ring–disk) from Pine Instruments were used as the counter electrode, reference electrode and working electrode, respectively. The working electrodes were constructed using the configuration proposed by Paulus et al. [27], and 1 mol L^{-1} NaOH (Merck) was used as the supporting electrolyte. An EDI101 rotator and a CTV101 speed control unit were also used. The electrode rotation rate was varied from 100 to 3600 rpm, and the experiments were controlled via the General Purpose Electrochemical System (GPES) software.

For these experiments, the electrolyte was first saturated with oxygen for 40 min, and oxygen flow was maintained over the electrolyte until the end of the experiments. The measurements were performed at a fixed scan rate of 5 mV s^{-1} and at room temperature.

2.2.3. Gas-diffusion electrodes

Given that the rotating ring–disk technique provides an indication of H_2O_2 production, gas-diffusion electrodes containing the best vanadium oxide electrocatalyst were produced after theses analyses and were used in an electrochemical cell, as proposed by Forti et al. [28], to determine the actual amount of H_2O_2 produced during exhaustive electrolysis at different potentials. The amount of H_2O_2 produced can be quantified by reacting the H_2O_2 just obtained in the electrochemical cell with 2.4×10^{-3} mol L^{-1} of $(NH_4)_6Mo_7O_{24}$ in 0.5 mol L^{-1} H_2SO_4, which produces a pale-yellow compound, i.e., a peroxymolybdate complex. The concentration of this complex can be determined by UV–Vis measurements at a wavelength of 350 nm, as proposed by Chai et al. [29] and by Forti et al. [30]. The amount of H_2O_2 produced was determined using a Varian Cary 50 spectrophotometer and a previously constructed analytical curve.

2.2.4. Analysis of vanadium dissolution

The GF AAS measurements were performed with a Zeenit 600 (Analytik Jena AG, Jena, Germany) equipped with a V hollow-cathode lamp (operated at 4.0 mA, with a spectral bandpass of 0.8 nm and a wavelength of 318.4 nm), a transversely heated graphite tube atomizer and a Zeeman background corrector. Argon (99.998%, v/v) was used as a purge gas. All measurements were performed using integrated absorbance (peak area) and were conducted in triplicate.

Aliquots containing 20 µL of the sample were added to the graphite platform. The pyrolysis and atomization temperatures were investigated in the ranges of 800–1800 °C and 2200–2700 °C, respectively. Vanadium determinations performed using the optimized temperature program are presented in Table 1.