Electrochimica Acta 291 (2018) 328–334

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

In-situ electrochemical activation of carbon fiber paper for the highly efficient electroreduction of concentrated nitric acid

Weikang Zhu [a], Xiangwen Zhang [a], Yan Yin [b], Yanzhou Qin [b], Junfeng Zhang [b, *], Qingfa Wang [a, **]

[a] Key Laboratory for Green Chemical Technology of the Ministry of Education, Tianjin University, 135 Yaguan Road, 300350, Tianjin, PR China
[b] State Key Laboratory of Engines, Tianjin University, 135 Yaguan Road, 300350, Tianjin, PR China

ARTICLE INFO

Article history:
Received 20 July 2018
Received in revised form
5 August 2018
Accepted 21 August 2018
Available online 20 September 2018

Keywords:
Carbon fiber paper
In-situ electrochemical activation
Nitric acid reduction
Metal-free electrode

ABSTRACT

An in-situ electrochemical activation method was developed to activate the carbon fiber paper (CFP) for the highly efficient concentrated HNO_3 reduction. The defects and heteroatoms were introduced onto the surface of carbon fiber resulting in a significant improvement in the reactivity. Furthermore, the surface wettability of electrode was adjusted to enhance the accessibility of the active surface. Owing to these advantages, the activated-CFP electrode exhibits a higher current density (464.1 mA cm^{-2}) for the electroreduction of 4 M HNO_3 compared to the conventional Pt electrodes (75.39 mA cm^{-2}). Based on scanning electron microscopy, Raman spectroscopy, X-ray photoelectron spectroscopy and contact angle analysis, the HNO_3 reduction mechanism on the activated CFP electrode was discussed. High activity as well as excellent electrochemical and chemical stability in the concentrated HNO_3 make the activated-CFP as an effective alternative for noble-metal electrode in the future industrial applications.

1. Introduction

Nitrate pollution of groundwater, the main drinking water source, is becoming a global problem. Developing advanced nitrate reduction strategies is necessary to address this problem. Concentrated HNO_3 effluents (2.0–7.0 M) discharged from the metallurgical industry [1] and high-level radioactive wastes [2] attract increasing attention. The best available technologies for nitrate-contaminated water treatment include reverse osmosis, electrodialysis, ion exchange, catalytic reduction and electrocatalytic reduction [3]. In recent years, electroreduction method is considered to be a more realistic alternative for nitric acid degradation due to its convenience, environmental friendliness and low cost [4–6]. During electroreduction process, nitrite and ammonia are the dominated products in neutral or basic electrolyte, while hydrazine and hydroxylamine are the products in weak acids [5]. In strong acids, oxynitride gases such as NO, N_2O, NO_2 become the main products of electroreduction [6,7]. As the important intermediates [8], NO and N_2O can be easily converted to the non-poisonous nitrogen via selective catalytic reduction (SCR) [9,10].

Achieving high performance for the nitric acid reduction reaction in terms of selectivity and reaction rate strongly depends on the rational design of electrodes. Different types of metal, such as Ni [11], Cu [12], Pt [13], Pd [14], Ti [12] and Rh [15] have been utilized as nitrate electroreduction catalysts. However, these non-noble metal catalysts are readily corroded, especially in the presence of concentrated HNO_3. On the other hand, noble metal catalysts, while generally effective, significantly increase the cost of the electrode, making the concentrated HNO_3 electroreduction process scale up challenging. Therefore, the development of efficient and chemically stable electrodes for electroreduction of concentrated HNO_3 is an urgent necessity.

Recently, carbon materials, having abundant defect sites as well as heterogeneous atoms, have been widely used as cathode materials for oxygen reduction, [16,17] and they exhibit a strong catalytic reduction activity with excellent stability. This provides a useful insight for the design of electrodes for electroreduction of concentrated HNO_3. However, established methods to increase the amount of defect sites or heterogeneous atoms, such as chemical vapor deposition (CVD) [18–20], physical vapor deposition (PVD) [20], plasma etching technology [21,22], heat treatment [23–25],

* Corresponding author. State Key Laboratory of Engines, Tianjin University, 135 Yaguan Road, 300350, Tianjin, PR China.
** Corresponding author. Key Laboratory for Green Chemical Techology of the Ministry of Education, Tianjin University, 135 Yaguan Road, 300350, Tainjin, PR China.
E-mail addresses: geosign@tju.edu.cn (J. Zhang), qfwang@tju.edu.cn (Q. Wang).

https://doi.org/10.1016/j.electacta.2018.08.127
0013-4686/

direct current arc-discharge [26] are frequently complicated. As a facile and effective method, electrochemical activation approach has been applied to modify the commercial carbon materials. It has been reported that the electrochemical performance of carbon fiber can be improved via electrochemical activation in acid (HNO_3 [27] or H_2SO_4 [28]) and neutral [29] solution. However, these activation processes are conducted at high potential [29], large anodic current [28] or in the condensed acid solution [27], resulting in the rigorous corrosion of carbon fibers. Thus, it is still a challenge to effectively activate the carbon fiber while maintaining its network via controlling electrochemical activation condition.

In our previous study, [13] nano-Pt supported on carbon fiber paper shows a high performance for the electrochemical reduction of concentrated HNO_3 with oxynitride gases released as the main product which can serve as a strong oxidizing agent [30] during anodic oxidation process. In order to improve the electrochemical performance of CFP for concentrated HNO_3, the CFP was activated in 4 M HNO_3 via cyclic voltammetry (CV) in the different potential range. To the best of our knowledge, the present work is the first example of in-situ activated-CFP applied as a cathode for the electrochemical reduction of nitric acid. It shows a high activity and stability, suggesting it has very good potential for replacing noble metal-based electrodes in industrial applications.

2. Experimental

2.1. Preparation of working electrode

The carbon fiber paper (CFP, 0.19 mm thickness, Toray) was cut into 1×2 cm^2, and then the fragments were heated in 1 M KOH for 2 h at 60 °C. After heat-treatment, 30 min ultrasonication was conducted to obtain the clean CFP fragments. The electrochemical experiments were conducted in a standard three-electrode glass cell with a carbon fiber beam and an $Hg/Hg_2SO_4/K_2SO_4$ (Sat.) (SSE, 0.616 V vs RHE) as the counter electrode and the reference electrode, respectively. Potential control was performed with an Autolab 302 N potentiostat/galvanostat. The CFP electrode was activated in 4 M HNO_3 solution by cyclic voltammetry (CV) from −0.5 V to 1.30, 1.35 or 1.40 V (vs SSE) for 12 cycles at a scan rate of 10 mV s^{-1}, and abbreviated as NCFP-1.30, NCFP-1.35 and NCFP-1.40, respectively.

2.2. Electrochemical test

The double-layer capacitance was measured at different scan rates (10, 20, 30, 40, 50 mV s^{-1}) in 0.5 M H_2SO_4. The electroreduction performance test was conducted in 4 M HNO_3 solution by CV from −0.65 V to 0.60 V (vs SSE) at 5 mV s^{-1}. The electrochemical impedance spectroscopy (EIS) was recorded in 4 M HNO_3 at 0 V vs OCP. The resistance (R) of CFP and activated-CFPs is obtained by measuring the current (I) and voltage (E) via an electrochemical workstation and a fixture with two electrodes (as shown in Fig. S10a) between −0.2 and 0.2 V at 50 mV s^{-1}. All measurements were carried out at 25 °C.

2.3. Characterizations and measurements

Field emission scanning electron microscope (FE-SEM) images were performed on a S-4800 FE-SEM (HITACHI) at an acceleration voltage of 5 kV, and the relative amount as well as distribution of C, N and O elements were obtained by an energy dispersive X-ray detector (EDX) attached to FE-SEM. X-ray diffraction (XRD) patterns of CFP and activated-CFPs were obtained on a diffractometer (RIGAKU D/max 2500) using the Cu Kα radiation (k = 0.15418). X-ray photoelectron spectra (XPS) patterns were recorded using an X-ray Photoelectron Spectrometer (Kratos Axis Ultra DLD) with an aluminum (mono) Kα source (1486.6 eV). Atomic force microscopy (AFM) images were obtained via a XE-70 AFM (Park) at non-contact mode. Fourier-transformed infrared (FT-IR) spectroscopy was measured by a Bruker Tensor 27 using the diamond lens Attenuated Total Reflectance (ATR) module. To investigate the products during the nitric acid reduction, the process was conducted in an H-type electrolytic cell (Tianjin Aida HengSheng Science & Technology Development Co., Ltd.) connected by glass sand core, and the gases were online detected by a mass spectrometry (OmniStar GSD320, Pfeiffer) with the gas flow rate of 2 mL min^{-1}. Contact angle measurements were conducted with a DSA100 drop shape analyzer (KRÜSS) at room temperature. A liquid droplet of 3 μL ultrapure water was carefully deposited onto the sample surface. The image of static contact angle was taken within 3 s after liquid droplet was contacted with the sample by a charge coupled device (CCD) camera. The contact angle was calculated by the Young-Laplace fit.

3. Results and discussion

The activation of commercial CFP was conducted in 4 M HNO_3 by cyclic voltammetry scanning from −0.5 V to 1.30, 1.35 or 1.40 V (vs SSE), and abbreviated as NCFP-1.30, NCFP-1.35 and NCFP-1.40, respectively. During the scanning process, the reduction peak shifted positively to 0.1 V (vs SSE) after eight cycles (as shown in Fig. S1), indicating an increase in the reduction kinetics. With continually increasing the number of cycles, the current density of this reduction peak rapidly increased and reached a maximum after 12 cycles. Therefore, the activation of all samples investigated in this study was performed under this condition. The morphology of the samples before and after activation were characterized by field emission scanning electron microscope (FE-SEM, Fig. 1a–d) to investigate the possible destruction of the carbon fiber network. Compared to the pristine CFP (Fig. 1a), the three-dimensional structures of NCFP-1.30 (Fig. 1b), NCFP-1.35 (Fig. 1c) and NCFP-1.40 (Fig. 1d) are completely preserved, indicating that the mechanical properties of the activated-CFPs are apparently unaffected. The microscopic changes of the carbon fiber surfaces were further characterized by atomic force microscopy (AFM). Fig. 1e–h shows the AFM images of commercial carbon fiber and electrochemically activated carbon fibers. The surface of pristine carbon fiber is relative smooth. After activation, deep grooves and stripes are formed on the surface of the carbon fiber. Linear analysis of typical AFM images (Figs. S2 and S3) exhibits a much higher roughness of NCFP-1.40 (about 932 nm) than that of the commercial CFP (about 350 nm), implying that the electrochemical activation process can increase the amount of pitting (e.g. structural defects, edges), which are commonly regarded as the active sites in the electrochemical catalytic process [31,32]. The SEM-EDX element mappings (Fig. 1i) show that heteroatoms (O and N) are distributed homogeneously on the surface of carbon fibers, indicating that the activation proceed on the whole CFP.

Changes in the graphitic structure and defects were analyzed by X-ray diffraction (XRD) and Raman spectroscopy. As shown in Fig. 2a, both the CFP and the activated-CFPs display two diffraction peaks at 25.6° and 54.9° corresponding exactly to the (002) and (004) planes of hexagonal graphite (JCPDF No. 41–1487). Compared with commercial CFP, the (002) peak of the activated-CFPs are broadened and weakened, suggesting a high number of defects on the surface of the fiber [27]. In the Raman spectrum (Fig. 2b), the D- and G-bands are related to the vibration modes of disordered and sp^2 carbons, respectively [29]. The 2D band is attributed to the second order Raman vibration modes, indicating a highly ordered structure with graphene-like domains [33]. The intensity and position of D, G, 2D as well as D/G peak intensity ratio (I_D/I_G) are