Highly efficient Pd-Fe/Ni foam as heterogeneous Fenton catalysts for the three-dimensional electrode system

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Abstract

A novel particle electrode (PE) Pd-Fe/Ni foam was synthesized and used for Dimetridazole (DMZ) degradation in the three-dimensional electrode (3D) system. Results showed that Pd-Fe/Ni foam exhibited excellent electrocatalytic activity and satisfactory electrocatalytic stability. Inducing Pd and Fe species could not only decrease the resistance and accelerate the electron transfer, but also cause synergistic effect. In the 3D system with Pd-Fe/Ni foam PEs, DMZ degradation was much more efficient as compared with those using Ni foam PEs, Fe/Ni foam PEs and Pd/Ni foam PEs, owing to direct electrolysis, and efficient production of H_2O_2 and $\cdot OH$ of Pd-Fe/Ni foam PEs.

Keywords: Three-dimensional system, Pd-Fe/Ni foam, Heterogeneous Fenton catalyst, Synergistic effect

1. Introduction

The three-dimensional (3D) electrode has been attracting much attention recently

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since by placing a large number of particle electrodes (PEs) into the 3D reactor, charged microelectrodes could be formed and resulting in much larger interfacial electrode surface area and higher mass-transfer efficiency as compared to conventional two-dimensional (2D) electrodes [1]. The properties of PEs are crucial for the entire system, and activated carbon, metal particles, carbon aerogels and Ni foam are commonly used as PEs [2-5]. Among them, Ni foam has been widely used as a promising PEs due to its good electrical conductivity, well-developed porous structure and high catalytic activity [6]. Liu et al. [5] reported that Ni foam as PEs displayed good oxygen reduction activity in 3D electrode system, because it could activate molecular oxygen to generate $\cdot\text{O}_2^-$ via a single-electron transfer pathway and subsequently generated H_2O_2 , and afterwards, $\cdot\text{OH}$ was produced in the presence of Fe(II) (Eqs. (1) - (3)). However, the amount of H_2O_2 generated by Ni foam was limited. In this case, to achieve high efficiency, efficient carbonaceous materials should be employed as the cathode, and besides, Fe^{2+} should be added to the system to catalyze $\cdot\text{OH}$ production. Nevertheless, carbonaceous materials are costly and their mechanical stability is low; also, Fe^{2+} addition makes the process more complicated; which limited this kind of system for practical application.

It has been demonstrated that loading catalysts on PEs can improve catalytic activity [7, 8]. Recently, it was shown that Pd-based catalysts hold great potential in

direct synthesis of H_2O_2 from electro-generated H_2 and O_2 (Eqs. (4) - (6)), which greatly resolves the problems mentioned above [9, 10].

However, Pd has the drawbacks of possessing weak ability to catalyze H_2O_2 decomposition, being expensive, and difficult to recycle after treatment. Iron is a widely used Fenton catalyst since it is cost-effective, highly efficient and environmentally friendly [11]. Thus, modifying the noble metal such as Pd with iron to synthesize composite catalyst should be desirable. For instance, Qin et al [12] synthesized $\text{AuPd}/\text{Fe}_3\text{O}_4$ nanoparticles as PEs, and their results showed that $\text{AuPd}/\text{Fe}_3\text{O}_4$ nanoparticles electrodes possessed preferable electrochemical properties for in situ supplement of H_2O_2 and releasing of Fe^{2+} , which activated Fenton-like reaction and thereby enhanced the degradation of pollutants. However, it should be noted that nanoparticles tend to aggregate, which would result in catalytic performance decline. Given this, supporting bimetallic Pd-Fe catalysts on support materials should be a more satisfied method.

In this study, we attempted to prepare novel Pd-Fe/Ni foam PEs, and use the as-synthesized PEs as effective multifunctional material in a 3D electrochemical reactor to combine the advantages of 3D reactor and Fenton-like reaction. Dimetridazole (DMZ) was chosen as the model compound for determining the electrocatalytic performance of the PEs. PEs characterizations were also performed.

2. Experimental

2.1. Preparation and characterization of Pd-Fe/Ni foam

Pd-Fe/Ni foam PEs were prepared by impregnation-calcination method followed by reduction process as previously reported [13, 14]. The PEs were characterized by FE-SEM, EDS, HRTEM, SAED, XRD, XPS, electrochemical impedance spectroscopy (EIS), linear scan voltammetry (LSV) and a surface area and pore size analyzer. The experiment details about preparations and characterizations of synthesized PEs are provided in supplementary materials.

2.2. DMZ degradation experiments

All experiments were performed in a 3D electrode reactor [15]. The anode and cathode were made of Pt sheets. Na₂SO₄ solution (5g/L) was used as the electrolyte. The concentration of DMZ solution was 50 mg/L, and a total volume of 400 mL was fed into the 3D electrode reactor. The initial pH was adjusted with 0.5mol/L H₂SO₄ or NaOH to 3. Compressed air with airflow of 1.0 L/min was sparged into the system during the experiment. PEs dose was 12.5 g/L, and a current density of 31 mA/cm² was applied to the 3D system.

Electrolytic degradations of DMZ in 2D, 3D system (with Ni foam, Fe/Ni foam, Pd/Ni foam and Pd-Fe/Ni foam as PEs, respectively) and two-compartment 3D system (separated by Nafion117 membrane and with Pd-Fe/Ni foam as PEs) were performed under the same conditions in the same reactor. Pd-Fe/Ni foam PEs adsorption of DMZ was carried out in the electrochemical reactor without applied current.

3. Results and discussion

3.1. Characteristics of particle electrodes

To demonstrate that bimetallic Pd-Fe catalysts have been successfully loaded on Ni foam, various characterizations were conducted. The raw Ni foam has a 3D network structure and the surface is relatively smooth (Fig.1a). For Fe/Ni foam, the surface is rough, and is coated with a “layer”, consisting of some irregular shape particles, demonstrating that Fe species have been successfully deposited on Ni foam (Fig.1b). Pd-Fe/Ni foam possesses large silk-like flaky structures, **resulting in larger specific surface area and more active sites for catalytic degradation**, which is in favor of catalytic activity (Fig. 1c) [16, 17]. Palladium and iron content of Pd-Fe/Ni foam are analyzed by EDS, and Pd and Fe amounts were 1.27wt% and 12.84 wt% (**Fig. S1**), respectively. **Fig. S2** shows EDS elemental mapping of Pd-Fe/Ni foam, which confirms that Pd, Fe and O elements are highly dispersed in the Pd-Fe/Ni foam PEs.

To further investigate the crystallization behavior of Fe or Pd-Fe catalysts, these catalysts stripped from Ni foam were analyzed by HRTEM and SAED. In Fig. S3, clear lattice fringes with a lattice spacing of 0.256 nm can be observed. SAED patterns of Fe catalysts display several well-defined rings for the diffraction planes, suggesting good polycrystalline nature of Fe catalysts. The HRTEM image (Fig. S3) denotes a lattice spacing of 0.235 nm, and Pd-Fe catalysts have good crystallinity with well-defined fringes.

The surface composition and metallic state of Pd and Fe of the Pd-Fe/Ni foam PEs were confirmed by XPS. As shown in **Fig. S4**, Ni, C, O, Fe, Pd elements can be

found on Pd-Fe/Ni foam PEs. High-resolution XPS spectra of Pd 3d and Fe 2p are shown in Fig. S4. The binding energies of near 335.5 and 340.6 eV belong to Pd 3d_{5/2} and Pd 3d_{3/2} peaks, which indicating that Pd species in Pd-Fe/Ni foam PEs are mainly metallic Pd. Except for Pd(0) species, another peak at 336.3 eV was also found, which can be assigned to Pd²⁺ in PdO. These results reflect the surface oxidation of Pd-Fe/Ni foam PEs due to exposure to air. The XPS spectra of Fe 2p depicts two characteristic peaks at 724.5 and 710.5 eV, which can be assigned to Fe 2p_{1/2} and Fe 2p_{3/2}, respectively. Two distinct bands centered at 710.3 eV and 713.2 eV, whose values are close to the range of Fe 2p_{3/2} binding energies of iron in FeO and Fe₂O₃ [18], could be observed from the deconvolution of the XPS spectra of Fe 2p_{3/2}, implying that the iron in our samples is present both as Fe²⁺ and Fe³⁺.

Fig. S5 shows the XRD patterns of Ni foam, Fe/Ni foam and Pd-Fe/Ni foam. Notably, all the samples showed typical diffraction peaks at 44.5°, 51.8° and 76.2°, corresponding to the (1 1 1), (2 0 0) and (2 2 0) planes of nickel metal (PDF No. 03-065-2865). No peaks for Pd and Fe were observed in Pd-Fe/Ni foam, which was likely due to lower amounts of Pd and Fe well-dispersed on the surface of Pd-Fe/Ni foam. Both EDS and XPS results discussed above confirmed that Pd and Fe were loaded on Ni foam. All the characterization results demonstrated that modified treatment of Ni foam PEs by bimetallic Pd-Fe catalysts have been successfully carried out.

3.2. Electrochemical activities of particle electrodes

The EIS was performed to examine the conductivity of PEs. Fig. 2 illustrates

Nyquist plots for various PEs. The inset shows the enlarged view of high frequency region. Each impedance spectrum presents a semicircle arc at the high frequency range and a straight line at the low frequency region for all PEs. The diameter of semicircle in high frequency area represents the charge-transfer reaction at the electrode/electrolyte interface, and the other located at low frequency region where a straight sloping line represents the diffusion of ions in all the PEs [19]. The arc curvature at high frequency region of Pd-Fe/Ni foam PEs was smallest, indicating that Pd-Fe/Ni foam PEs exhibited the smallest charge transfer resistance. This is likely due to the fact that loadings of Pd and Fe species on Ni foam could decrease the resistance and accelerate the electron transfer on the Pd-Fe/Ni foam interface. This may be helpful for the Pd-Fe/Ni foam PEs to enhance the electrochemical degradation of pollutants and further reduce energy consumption.

LSV is a useful tool for evaluating the electrochemical activities of PEs. The true DMZ decomposition current was the current difference between the one with and without DMZ with various PEs (Fig. 3). The actual current density of degradation DMZ with different PEs followed the order of Pd-Fe/Ni foam > Fe/Ni foam > Ni foam, implying that the Pd-Fe/Ni foam PEs had better electrochemical activity. This could be ascribed to the fact that the electronegativity of Fe(III) is 1.96 while that of Pd(0) is 2.20, thus reduction of Fe(III) to Fe(II) by Pd(0) is favorable, behaving as Lewis acid sites, which is beneficial for the interfacial electron transfer and improving activities [20, 21].

3.3. DMZ degradation and H₂O₂ accumulation

DMZ degradation results are shown in Fig. 4. For the adsorption experiment of Pd-Fe/Ni foam, only 4.2% DMZ removal was obtained, which was insignificant for DMZ removal. The limited adsorption ability of Pd-Fe/Ni foam was because of its small BET surface area ($1.488 \text{ m}^2/\text{g}$). When the 2D system was used, DMZ removal of 42.6% was attained. Meanwhile, using Fe/Ni foam or Pd/Ni foam in 3D systems, DMZ reduction of 78.1% and 63.0% were achieved, respectively, which reflected that Pd/Ni foam had inerter catalytic activity compared with Fe/Ni foam. A slightly improved DMZ removal efficiency of 82.3% was achieved in the two-compartment 3D system (with Pd-Fe/Ni foam as PEs). In a sharp contrast, almost 91.3% of DMZ was removed within 30 min by 3D Pd-Fe/Ni foam system and DMZ removal reached 96.5 % when the experiment was prolonged to 60 min. This implied that the addition of Pd and Fe species greatly improved electrocatalytic performance of Pd-Fe/Ni foam PEs. This was supposed to be closely related to the in-situ catalysis decomposition of the generated H_2O_2 into $\cdot\text{OH}$ during the process (discussed below), which could degrade DMZ more efficiently.

In the meantime, it was assumed that all the electrocatalytic degradation processes of DMZ followed pseudo-first order reaction kinetics. Time based rate constants (min^{-1}) were summarized in Table S1. In agreement with this degradation efficiency trend, the apparent rate constants of DMZ degradation in the whole 3D systems were higher than that in 2D system ($9.36 \times 10^{-3} \text{ min}^{-1}$). The rate constant (0.0566 min^{-1}) of 3D Pd-Fe/Ni foam system is much higher than that of 3D Fe/Ni foam system (0.0255 min^{-1}) and 3D Pd/Ni foam system (0.0155 min^{-1}), and even

more than 1.36 times of their sum (0.0411 min^{-1}). This significant enhancement of DMZ degradation suggested the existence of synergistic effect between Pd and Fe species in 3D Pd-Fe/Ni foam system. We have also investigated the Energy consumption (E_{EO}) in these electrocatalytic systems (Table S1). E_{EO} value for 3D Pd-Fe/Ni foam system was lower than other electrocatalytic systems. Thus 3D Pd-Fe/Ni foam system is more energy-saving and high efficient than the other processes.

Along with the degradation of DMZ, accumulations of H_2O_2 in different systems were determined. As shown in Fig. 5, negligible amount of H_2O_2 were detected for the cases of using Pd-Fe/Ni foam **adsorption system** and 2D system. In contrast, the concentration of H_2O_2 reached $61 \text{ }\mu\text{mol/L}$ in 3D Ni foam system; and the high accumulation of H_2O_2 in this system was because Ni foam could activate molecular oxygen to produce $\cdot\text{O}_2^-$ and subsequently generate H_2O_2 (Eqs. (1)-(3)) [5]. Notably, the addition of Pd markedly elevated concentration of H_2O_2 for Pd/Ni foam; the reason for this may be attributed to the fact that Pd species are favor for synthesis of H_2O_2 , yet have weak ability to catalyze H_2O_2 decomposition. When Fe was loaded on the Ni foam, H_2O_2 accumulation decreased dramatically compared with the case of 3D Ni foam system. This could be contributed to quickly decomposition of H_2O_2 to generate more reactive oxygen species (ROS) in the presence of Fe. While inducing both Pd and Fe species, H_2O_2 accumulation declined significantly since Fe species can catalyze the decomposition of H_2O_2 to produce more active $\cdot\text{OH}$, these were in line with DMZ degradations. Relatively low concentration of H_2O_2 was detected in

3D Pd-Fe/Ni foam system, since the detected amount was residual H₂O₂, thus the equilibrium concentration of H₂O₂ was not high. To emphasize the role of Pd in H₂O₂ formation, which may follow reaction (6), accumulations of H₂O₂ in the two-compartment 3D system separated by Nafion117 membrane (with Pd-Fe/Ni foam as PEs) were performed to prevent the H₂ formed on counter electrode get into the bulk electrolyte. The H₂O₂ concentration gradually increased to 7.62 μmol/L within the first 30 min, and reduced afterwards, and was lower than those from 3D Pd-Fe/Ni foam systems. These results proved that Pd catalyst could in-situ synthesize H₂O₂ with the presence of O₂ and H₂ producing by water electrolysis, and H₂O₂ could be directly decomposed into ·OH by Pd catalyst (Eq.(7)), which promote decomposition of organic pollutants [9].

As a summary, Pd-Fe/Ni foam PEs are both particle electrodes of 3D reaction system and catalysts of Fenton-like reaction, leading to efficient electrochemical degradation of DMZ in the 3D electrode system, as shown in Fig. S6.

3.4. Cyclic performance of Pd-Fe/Ni foam

The stability of Pd-Fe/Ni foam PEs over eight consecutive cycles for the degradation of DMZ was evaluated. After each run, Pd-Fe/Ni foam PEs were recycled by filtration and washed with distilled water and then dried at 70 °C for 5 h. Fig. S7 reveals that removal efficiencies of DMZ could steadily maintain at more than 90% after eight consecutive cycles, demonstrating that Pd-Fe/Ni foam PEs have excellent electrocatalytic durability. It should be noted that the leaching iron ions were below

0.5 mg/L (for eight consecutive cycles are 0.47, 0.42, 0.36, 0.30, 0.33, 0.27, 0.22, 0.18 mg/L, respectively), which were acceptable according to EU discharge standards [22].

4. Conclusions

In summary, a three-dimensional electrode system with synthesized Pd-Fe/Ni foam PEs was used to degrade DMZ. The PEs displayed excellent performances for DMZ removal with low energy consumption by direct electrolytic, in-situ production of H₂O₂, Fenton-like catalytic reaction, and synergistic effects between Pd and Fe species were exhibited. The electrocatalytic durability of the Pd-Fe/Ni foam over eight cycles indicated an outstanding recycling capacity for long-term electrocatalytic reaction. This study provides a new point on preparing high performance catalysts loaded on particles to improve the performance of 3D electrode technology.

Acknowledgments

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Figure captions

Fig.1 (a) The SEM images of Ni foam; (b) Fe/Ni foam; (c) Pd-Fe/Ni foam.

Fig.2 EIS plots of Ni foam, Fe/Ni foam and Pd-Fe/Ni foam PEs (Inset: the enlarged view of the high frequency region).

Fig.3 LSV (scan rate 50 mV/s) of Ni foam, Fe/Ni foam and Pd-Fe/Ni foam PEs in without DMZ solution and with 50 mg/L DMZ solution containing 5g/L Na₂SO₄ solution (pH=3).

Fig.4 The removal efficiency of DMZ in different systems.

Fig.5 The accumulation of the H₂O₂ in different systems.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5