

Advances in Carbon Felt Material for Electro-Fenton Process

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Abstract In electro-Fenton process, carbon-based materials, particularly 3D carbon felt, are the best choices for the cathodic electrodes because of several advantages such as low cost, excellent electrolytic efficiency, high surface area, and porosity. In this chapter, various aspects of this material are discussed in detail. This chapter is divided into three main sections, including (1) characterization of carbon felt (CF), (2) modification of CF, and (3) application of CF in electro-Fenton (EF) process to remove biorefractory pollutants. First of all, the typical characteristics of CF such as morphology, porosity, and conductivity are discussed. Next, in the modification section, we introduce different methods to improve the performance of CF. We especially focus on the surface area and electrochemical activity toward electrodes applications. Finally, both modified and non-modified CF is used as cathode materials for EF systems like homogeneous, heterogeneous, hybrid, or pilot-scale types.

Keywords Carbon felt, Conductivity, Electrochemical activity, Electro-Fenton process, Hydrogen peroxide production, Modification, Surface area

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Abbreviations

AHPS	4-Amino-3-hydroxy-2-p-tolylazo-naphthalene-1-sulfonic acid
ALD	Atomic Layer Deposition
AO7	Acid orange 7
APPJ	Atmospheric Pressure Plasma Jet
AQDS	Anthraquinone-2,6-disulfonate
BDD	Boron-doped diamond
BEF	Bio-electro-Fenton
CF	Carbon felt
CNT	Carbon nanotube
CTAB	Cetyl trimethylammonium bromide
CV	Cyclic voltammogram
CVD	Chemical vapor deposition
DCF	Diclofenac
DMF	<i>N,N</i> -dimethyl formamide
DO 61	Direct orange 61
EC	Energy efficiency
EF	Electro-Fenton
ENXN	Enoxacin
EPD	Electrophoretic deposition
FeAB	Iron alginate gel beads
GF	Graphite felt
GO	Graphene oxide
LDH	Layered double hydroxide
MCE	Mineralization current efficiency
MCF	Microbial fuel cell
MO	Methyl orange
N-doped	Nitrogen-doped
ORR	Oxygen reduction reaction
PAH	Polycyclic aromatic hydrocarbon
PAN-CF	PolyAcryloNitrile-Carbon Felt
PAN-GF	Polyacrylonitrile-graphite felt
PANi	Polyaniline
PB	Prussian blue
PCOC	4-Chloro-2-methylphenol

PEM	Proton Exchange Membrane
POP	Persistent Organic Pollutant
PPy	Polypyrrole
RF	Radiofrequency
rGO	Reduced graphene oxide
RTD	Residence Time Distribution
SCEs	Saturated calomel electrode
SEM	Scanning Electron Microscopy
SPEF	Solar Photo-electro-Fenton
SWCNT	Single-walled carbon nanotube
TOC	Total organic carbon
TT	Thermal treatment
VRFE	Vanadium redox flow battery
XPS	X-ray photoelectron spectroscopy
ZIF	Zeolitic Imidazolate Framework
ZME	Zeolite-modified electrode

1 Introduction

Owing to impressive properties such as low cost, excellent electrolytic efficiency, high surface area, and porosity and the ability to provide abundant redox reaction sites and mechanical stability [1–4], carbon felts (CF) are commonly used as electrodes. However, they simultaneously have some disadvantages relevant to their inadequate wettability and electrochemical activity in aqueous solutions because of their hydrophobic surface nature and poor kinetics for reduction and oxidation reactions. This partly declines the performance of pristine felts when they are applied at electrodes [5, 6]. In the effort to make the felt electrodes more active, several modification methods have been adopted at various conditions. Chakrabarti et al. [7] reported for instance some modification methods to improve the catalytic properties and the conductivity of CF electrodes such as deposition of metals and addition of functional groups by chemical and thermal treatments on the electrode surface. Several methods to produce vapor grown carbon fibers, carbon nanotubes (CNTs), or nitrogenous groups on the carbon fiber surface of CF electrodes were discussed [7]. After these modification processes, the electrochemical activity of CF could be remarkably enhanced [6, 8]. For wastewater treatment, CF was used widely as cathode materials for the removal of Persistent Organic Pollutants (POPs) in aqueous medium by electro-Fenton (EF) process. According to the review of Brillas et al., carbon electrodes present many advantages like nontoxicity, good stability, conductivity, and chemical resistance [9]. The efficiency of EF system using felt cathodes was studied in comparison with other materials like activated carbon fiber, reticulated vitreous carbon, carbon sponge, etc. [10–12]. In order to present a holistic overview about CF-based material for EF process, we will discuss in this chapter some important aspects of this material, including (1) the fabricating

methods and specific properties of pristine felt materials, (2) the various ways to modify felt electrodes, and (3) the application of CF-based cathodes for the removal of biorefractory pollutants by EF treatment. Importantly, modified EF systems using electrons produced from a green power source in fuel cell as well as EF pilot were investigated. These new technologies open new gates for application of felt materials in industrial areas toward zero-energy depollution.

2 Characterization of CF Material

CF is often observed under long smooth fibers dispersed randomly with homogeneous large void spaces between them (Fig. 1). Each fiber has cylinder-like shape with shallow grooves along the long axis which was formed by the combination of thinner fibers, melted together lengthways as reported by González-García et al. [14]. The addition or cutting of thinner sheets from the original one can change the thickness of the three-dimensional felt electrode. The geometrical shape of fibers is quite different from other materials, partly leading to various values for structural as well as physical parameters as shown in Table 1.

3 Method to Modify CF Material

3.1 Chemical Treatment

To activate the surface of felt materials, chemical treatment of CF is useful. Micropores could be generated by surface etching with KOH at high temperature ($\sim 800^{\circ}\text{C}$) leading to oxygen-containing functional groups. Furthermore, the activation by KOH improved remarkably the electrochemical activity of polyacrylonitrile-graphite felt (PAN-GF) (*Gansu Haoshi Carbon Fiber Co., Ltd.*) via the formation of these oxygen groups and the edge carbon sites [16]. The samples could be also treated by refluxing/

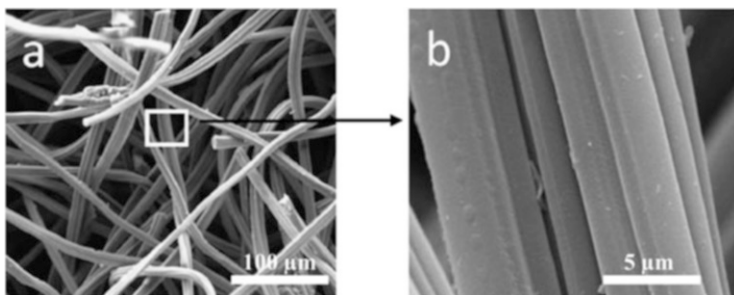


Fig. 1 (a, b) Scanning Electron Microscopy (SEM) images of CF at various magnifications. Reprinted from Deng et al. [13]. Copyright (2010), with permission from *Elsevier*

Table 1 Properties of CF electrodes according to the manufacturer [14, 15]

Company	Type	Porosity	Mean pore diameter	Specific surface area	Apparent electrical resistivity
		Value	Value (m)	Value ($\text{m}^2 \text{m}^{-3}$) excepted when mentioned	Value (Ωm)
Carbone-Lorraine	RVG 2000	0.95	–	–	3.5×10^{-3}
	RVC 1000	–	1.19×10^{-4}	31,000 ^a	–
	RVC 2000	–	2.57×10^{-4}	15,000 ^a	–
	RVC 4000	–	1.60×10^{-4}	23,500 ^a	–
	RVC 4002	0.84	2.94×10^{-4}	33,684 ^b 3,369 ^c	2.4×10^{-1d}
		0.984	0.12×10^{-4}	22,100–22,700 ^a (0.067–6) $\times 10^{7a}$	2.7×10^{-3e}
SiGRI	Sigratherm GFD 5	0.95	1.52×10^{-4}	24,000–60,000 ^a	–
Fiber Materials	CH (0.175)	0.86	1.56×10^{-4}	11,000 ^a	–
	CH (0.25)	0.90	2.04×10^{-4}	8,800 ^a	–
Amoco Thornel Mat VMA		0.98	6.37×10^{-4}	–	7.14×10^{-3}
Shanghai Energy Carbon Limited Co., China	–	–	–	$0.33 (\text{m}^2 \text{g}^{-1})^f$	–

– Not determined

^aCalculated from Filamentary analog^bCalculated from mercury porosimetry^cCalculated from Residence Time Distribution (RTD) modeling^dValue for the short direction^eValue for the long direction^fCalculated from Physical gas adsorption isotherm

boiling either in sulfuric or nitric acid or in their mixture in order to fabricate felts with a large amount of chemisorbed oxygen on the surface [17, 18]. In fact, the better electrochemical property of GF was observed in the higher acid concentration [19]. The increased electrocatalytic activity of the treated GF was thus attributed to the increased concentration of C–O and C=O functional groups on the surface. The combination between thermal and chemical treatments is sometimes necessary to improve the efficiency of the treatment [20]. Electrochemistry is also an interesting route for the growth of functional group. It requires the application of constant current or potential in acidic solutions like $1 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$. The modification following the electrochemical oxidation was successfully applied to improve the properties of different felts like GF (*Shanghai Energy Carbon Limited Co., China* [15] or *Sanye Carbon Co., Ltd.* [21]). Apart from acidic treatments, low-cost chemical reagents like ethanol and hydrazine hydrate were applied to chemically modify the graphite. Interestingly, after modification, some carbon nanoparticles and oxygen/ nitrogen-containing functional groups appeared simultaneously on the cathode surface, which

greatly improved the hydrophilicity of the surface and the electrocatalytic activity. Contact angles decreased gradually from 141°, to 123°, to 110° for bare GF (*Shanghai Qijie Carbon Material Co., LTD*), GF-ethanol, and GF-ethanol/hydrazine, respectively [22, 23].

3.2 Thermal and Plasma Treatment

The thermal treatment under gas flow containing oxygen and/or nitrogen is a simple way for felt modification to improve the electrochemical properties and the hydrophilicity [8]. In the study of Zhong et al. [24], a significant enhancement of the electrochemical activity was observed on GF, based on rayon or PAN precursors after thermal treatment under air. It was found that the electrical conductivity of the PAN-based felts was superior to that of its rayon-based counterpart. X-ray photoelectron spectroscopy (XPS) analysis pointed out that the rayon-based felts reacted more easily with oxygen and forms C=O groups, while the PAN-based felts were more resistant to oxidation and preferentially form C–O groups. The more extensive oxygen interaction in the rayon felts was thought to be due to its microcrystalline structure. Thermal treatment of GF electrodes was carried out under NH₃ atmosphere at 600°C and 900°C. The nitrogen-doped (N-doped) felt was fabricated with high electrochemical performance attributed to the increased electrical conductivity, the increase of active sites amount, and the improved wettability provided by the introduction of the nitrogenous groups on the surface of GF [25, 26]. Interestingly, the thermal treatment under air can also improve the surface area of the pristine electrodes: after treatment in air at 400°C, the surface area of the modified felts increased by more than ten times in comparison to the pristine one based on rayon (*SGL*, thickness 3 mm) [27]. This value was 1,344% higher than bare PAN-CF (*Nippon Chem*, thickness 3 mm) [5]. In the same way, thermal treatment under a flux of N₂/O₂ with 1% of oxygen at 1,000°C for 1 h could also increase the S_{BET} of commercial felts (*Johnson Matthey Co., Germany*, thickness 1.27 cm) up to 64 m² g⁻¹, i.e., around 700 times higher than raw samples. As further benefit, the crystalline size was also ameliorated due to the selective etching of amorphous carbon by thermal treatment [28].

Plasma treatments are also carried out to perform the growth of oxygen-containing functional groups or/and nitrogen doping on the surface of fibers. Oxygen plasma treatment was conducted in a radiofrequency (RF) plasma set-up controlling treatment time, power of the RF generator, and oxygen pressure. In 2015, Chen et al. [29] reported the modification of felts (*COS1011, CeTech, Taiwan*, thickness 6 mm) with Atmospheric Pressure Plasma Jets (APPJs). The APPJ treatment was performed on the felts under the single spot and scanning modes with the presence of N₂ flow rates. The formation of specific oxygen functional groups was observed after the plasma treatment. XPS revealed that this method rather favored the formation of C–O groups than C=O groups [27]. However, the plasma treatment process only often increases the amount of functional groups on

felts and not remarkably the surface area. Apart from oxygen-containing functional groups, nitrogenous groups can also improve electrocatalytic activity of carbon electrode materials for redox reactions. This comes from the reason that carbon atoms neighboring nitrogen dopants present a high positive charge density improving their electrocatalytic activity [30]. Furthermore, nitrogen doping can also make CF materials more hydrophilic which increases the electrochemically active sites [25]. Briefly, the increased amount of surface-active oxygen and nitrogenous groups by thermal or plasma treatment can enhance electrochemical performance of the modified material through facilitating charge transfer between felt electrodes and electrolytes [27, 31].

3.3 Graphene Based Modification

Graphene has received extensive attention due to its remarkable electrical, physical, thermal, optical, high specific surface area, and mechanical properties [32, 33], and it is then widely applicable for electrochemical applications [34]. Dip-coating, electrophoretic deposition (EPD), or voltamperometric techniques are methods often used separately or combined together for the coating of graphene-based materials on felt electrodes. For example, the coating of reduced graphene oxide (rGO) on CF (*Shanghai Qijie Carbon Co., Ltd.*) was performed using different steps: (1) Graphene oxide (GO) suspension was prepared by sonication in water for 1 h to exfoliate graphite. (2) GO was loaded on the CF surface by the dipping-drying process. (3) The GO was then electrochemically reduced by applying a constant voltage in 0.5 M Na₂SO₄ for 10 min. By comparing the response of cyclic voltammograms (CVs) curves in 0.5 M Na₂SO₄ solution, the rGO/CF electrode has overall a higher current density than the bare CF over the scanned voltage range (−0.6 to 0.6 V), suggesting a larger electrode surface area and better conductivity after modification [35].

In addition, the EPD shows several advantages for obtaining homogeneous films on felt electrodes from suspensions containing well-dispersed charged particles like GO solution, with high deposition rates, simple operation, easy scalability, and all that by avoiding the use of binders [36]. A graphene-modified GF was synthesized using EPD method by applying a voltage of 10 V for 3 h. The negative GO sheets were moved toward the positive GF electrode. The electrode showed graphene-like sheets on the fiber surface either in a wrinkled configuration or anchored between them. These sheets consisted of partially rGO with oxygen content decreasing from 13 at.% in the initial GO to 3.84 at.%. To compare with other modification methods, the chemical treatment by electrochemical oxidation in 1 M H₂SO₄ (GF-H₂SO₄) for 3 h or thermal treatment (TT-GF) at 450°C with the same time, 3 h, under air flow in a tubular furnace was done. The electrochemical performance of graphene modification was even higher than GF-H₂SO₄ or TT-GF [37]. Because of the excellent electrochemical properties of graphene-based materials, they have still a promising future for applications in the modification of CF electrode.

3.4 Carbon Nanotube-Based Modification

Felt electrodes were attractively modified by carbon nanotubes because of their excellent electrical and thermal conductivities, mechanical flexibility, and significantly large surface area [38]. The coating of single-walled carbon nanotube (SWCNT) was performed by a simple way where CF was immersed into the SWCNT suspension. The CF was then dried at 80°C for 5 h. The SWCNT (2 wt% relative to the amount of carbon felt) was ultrasonically dispersed previously in *N,N*-dimethyl formamide (DMF). The process was repeated until all the SWCNT suspension adsorbed into the CF. The modified electrode showed a better catalytic performance with higher electron transfer rate compared to the raw one [39]. On the other hand, the carbon nanotubes (CNTs) could be directly grown on the surface of felts by chemical vapor deposition (CVD) method without binding agent. For this purpose, the felt sample was placed in the center of a quartz tube and heated at high temperature (around 800°C) under Ar gas flow, followed by the injection of the carbon precursor source. Toluene or ethylenediamine was applied as source solution for the growth of CNTs or nitrogen-CNTs on GF. The small size (~30 nm in diameter) of CNTs created a significant increase of the electrochemical surface area of the felt materials. In addition, the N-doping could further improve the electrode performance because of the modified electronic and surface properties of CNTs on GF [40]. The CNTs/CF electrode was also obtained by growing CNTs via CVD of methanol on cobalt and manganese metallic particles deposited on CF. The specific surface area of CF loaded with 37.8 mg of CNTs was found to be 148 m² g⁻¹ instead of 1.0 m² g⁻¹ for non-modified one [41].

Growth of multi-walled carbon nanotubes (MWCNTs) on CF was investigated by CVD using ferrocene in toluene as precursor (Fe(C₅H₅)₂ at 20 g L⁻¹ in C₇H₈). CNTs with high aspect ratio were grown from the iron sites, generated by the decomposition and the subsequent nucleation of the iron species from the ferrocene precursor deposited on the CF substrate. The specific surface area successively increases with an increase in CNT loading and reaches 150 m² g⁻¹ for a CNT weight intake of 98%. A significant enhancement of mechanical strength and electrical conductivity along with the effective surface area was observed. The residual iron catalyst was removed by an acid treatment (HNO₃, 65%, at 80°C for 2 h), which caused the formation of oxygenated functional groups on the CNT surface [42]. Other CNTs/CF electrodes were prepared using the decomposition of methanol on different metallic catalysts, including cobalt, manganese, and lithium, supported on CF [43]. Bamboo-like structures were identified in good agreement with the study of Rosolen et al. [44].

EPD shows noticeable advantages as a low-cost and simple method compared to CVD [45, 46]. The first step is the dispersion of CNTs in isopropyl alcohol for 3 h in ultrasonic bath at 1.6 g L⁻¹. Applying a constant voltage of 40 V for 60 s, 1.05 wt% CNTs were deposited uniformly on CF with no obvious agglomeration or acutely curly body [47]. The studies have been enlarged with CNTs functionalized with carboxyl and hydroxyl groups. The carboxyl MWCNTs were adhered onto the CF

(Shenhe Carbon Fibre Materials Co. Ltd., thickness 4 mm) by immersing in a mixture solution of COOH-MWCNTs containing 0.02 wt.% Nafion as a binder to guarantee the stability of the MWCNTs/CF electrode. Not only the hydrophilicity but also the number of active sites of CF was upgraded, depending on the carboxyl groups of MWCNTs [48]. Similarly, the COOH-MWCNTs were ultrasonically dispersed in dimethyl formamide and then the CF was immersed in this solution. COOH-MWCNTs/CF was obtained by drying the electrode in the oven at 100°C for 24 h [49].

3.5 Polymer-Based Modification

Polyaniline (PANi) and polypyrrole (PPy) are the most common conducting polymers for electrode modification because of their high electrical conductivity, ease of preparation, and environmental stability [50, 51]. The coating of conductive polymer film on the surface of CF is usually conducted by the electropolymerization process in solution containing monomers. Interestingly, electropolymerized materials have unique properties which are not peculiar to the corresponding monomers [52, 53]. The PPy/anthraquinone-2,6-disulfonate (AQDS) conductive film was coated on CF (Liaoyang Jingu Carbon Fiber Sci-Tech Co., Ltd., China) (Fig. 2c) in a basic three-electrode electrochemical cell. The polymer film was formed on the CF surface by applying a constant potential of 0.8 V vs saturated calomel electrode (SCE), controlling the thickness with the coulometry. The modified electrode resulted in larger current responses when compared to the unmodified electrode (Fig. 2e) due to the enhanced surface area and conductivity of the PPy/AQDS-modified electrode [54]. Besides electropolymerization method, the polymer-modified felts could be prepared in a simple way by submerging CF in HCl solution adding aniline monomer and ammonium persulfate. The polymerization was conducted for 8 h by continuously stirring in order to coat PANi on the surface of CF [56].

In order to improve the physicochemical and electrochemical properties of the conducting organic films, many copolymers were prepared and investigated. The electrochemical activity of poly(aniline-co-*o*-aminophenol) was about four times as high as that of PANi 0.3 mol L⁻¹ Na₂SO₄ solution of pH 5. The copolymer had a good stability and a high reversibility [57]. A poly(aniline-co-*o*-aminophenol) film with average mass at 1.17 ± 0.1 g was deposited on CF by Cui et al. [39] through electrochemical synthesis in solution containing simultaneously aniline and *o*-aminophenol. What's more, the biocompatibility of felt electrodes was increased significantly when they were coated by the co-polymers containing nitrogen/oxygen functional groups. The hydrophilic conductive co-polymers like poly (aniline-co-*o*-aminophenol), poly (aniline-co-2, 4-diaminophenol), and poly (aniline-1, 8-diaminonaphthalene) acted as the bridge or mediator, playing the role of bonding bacteria and CF cathode more tightly, and facilitated or improved the electron transfer process from cathode to bacteria for microbial fuel cell application [56]. In terms of the increase of surface area, electronic conductivity, biocompatibility, and

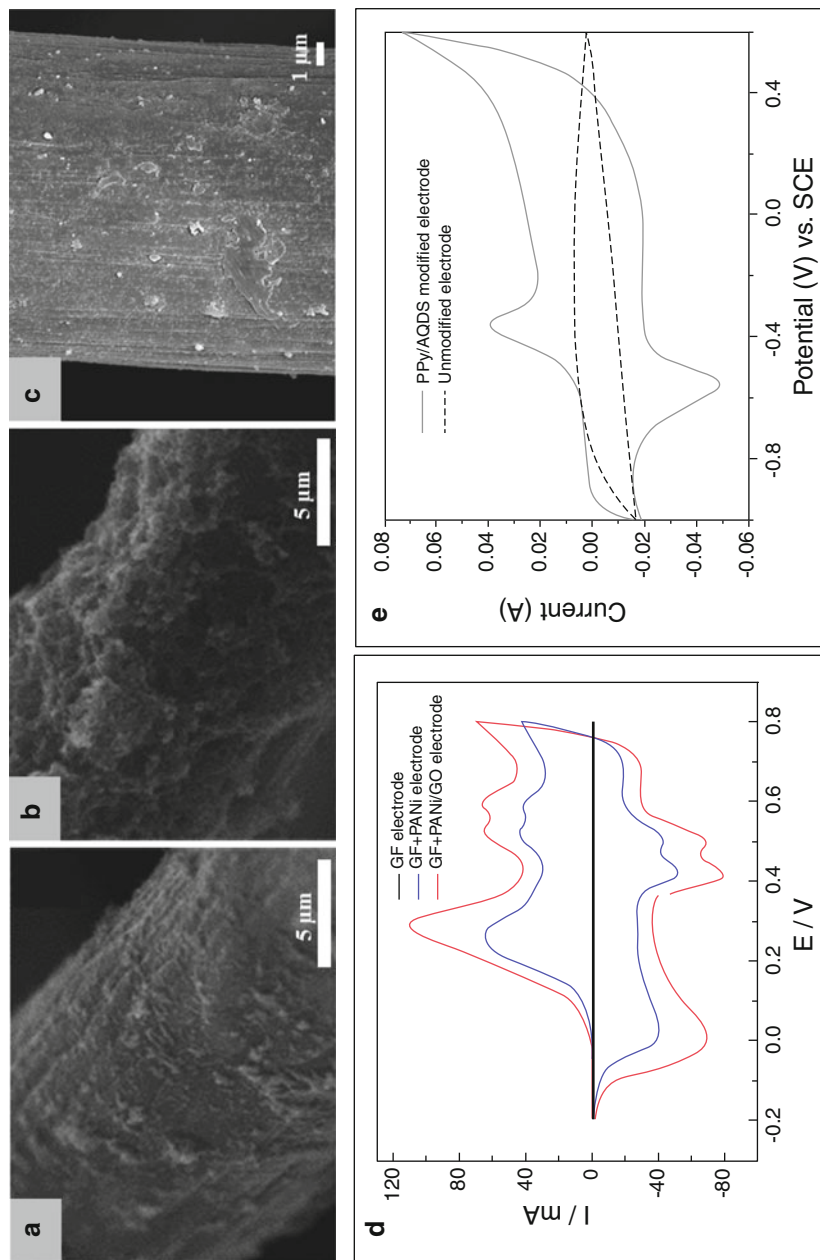


Fig. 2 SEM images of (a) PANi/GF; (b) PANi/GO-GF, (c) PPy/AQDS-CF; CVs of the modified electrodes in (d) 1.0 mol L⁻¹ H₂SO₄ solution (Scan rate of 5 mV s⁻¹), and (e) 0.1 mol L⁻¹ phosphate buffered solution (pH 7.0) (Scan rate of 10 mV s⁻¹). Reprinted from Feng et al. and Jiang et al. [54, 55]. Copyright (2010, 2015), with permission from *E/sevier*

stability, PPy was simultaneously covered on the GF (Beijing Sanye Co. Ltd., thickness 5 mm) with GO. The growth of PPy/GO on GF electrode was carried out in one step by electropolymerization of pyrrole (Py) in the solution containing simultaneously the GO. The functional groups of GO like $-OH$ and $-COOH$ play the role of external dopant for PPy formation. The new electrode exhibited improved performance compared with PPy alone when it could increase significantly the power density of Microbial Fuel Cell (MFC) [58]. In order to overcome the unsatisfactory stability of PANi-modified GF electrode, GO was introduced into PANi/GO composite for the modification of graphite (*Chemshine Carbon CO., China*) by one electrochemical approach [59]. The PANi/GO-GF (Fig. 2b, d) enhanced outstandingly the electrochemical activity as well as the hydrophilicity of GF electrode. The stability of new electrode was actually noticeable when after 1,000 s, the oxidation current of the PANi/GO-modified GF electrode was still higher than that of the PANi-modified GF electrode (Fig. 2a) because of the synergistic effect of PANi and GO [55]. Moreover, conductive polymers have been combined with CNTs to increase the effective surface area and the electrical conductivity of the resulting material. The PANi was electropolymerized on the surface of GF (*Beijing Sanye Carbon, China*, thickness 4 mm) followed by the EPD of CNTs [60]. Using polymer for the modification of GF electrode is convenient and effective method because it is a low-cost approach and improves the electrochemical performance.

3.6 Zeolite-Based Modification

Zeolites are porous crystalline aluminosilicates of SiO_4^{4-} and AlO_4^{5-} tetrahedra connected by oxygen bridges. Zeolite-modified electrodes (ZMEs) have numerous applications in various fields especially in electroanalytical chemistry because of the unique molecular sieving properties of zeolites [61]. NaX zeolite consists of sodalite cages arranged in a three-dimensional open framework leading to a microporous crystalline structure. Cages are linked through double six rings creating a large super cage cavity [62]. NaX zeolite was grown on GF during hydrothermal synthesis at $100^\circ C$ for 3 h in solution containing sodium silicate, sodium aluminate, and sodium hydroxide with a molar composition of 3.5 Na_2O :1 Al_2O_3 :2.1 SiO_2 :1,000 H_2O . Electrode activity was investigated in the presence of bacterial to prove the interest of the approach for microbial biofuel cells. The GF modified with NaX showed a higher electrochemical activity after ex situ acclimatization compared to bare electrodes [62, 63].

Prussian blue (PB, ferric hexacyanoferrate) is another kind of zeolite interesting for electrode modification [64, 65]. PB and its analogues have been known as polynuclear transition metal hexacyanometalates that own the zeolite-like structure [65–67]. Its electrochemical behavior was reported for the first time in 1978 by Neff et al. [68]. Some years later, the PB has attracted extensive attention due to its features relevant to inherent electrochromic [69], electrochemical [70], photophysical [71], as

well as molecular magnetic properties [72]. The electrochemical and chemical depositions were used to modify the GF electrode by PB. Firstly, the conductivity of felt electrode was improved via the electrodeposition of Platinum (Pt) on the surface of GF, which also played the role of catalyst for PB formation. Secondly, the Pt/GF electrode was immersed for 60 min into 20 mL of a solution containing 1.0 mmol L^{-1} FeCl_3 , 1.0 mmol L^{-1} $\text{K}_3\text{Fe}(\text{CN})_6$, 0.1 mol L^{-1} KCl , and 0.025 mol L^{-1} HCl . Next, the washing step was repeated many times before drying the electrode for 2 h at 90°C . This sample was noted as PB@Pt/GF. The SEM images of PB@Pt/GF showed the successful deposition of PB on the GF. PB@Pt/GF electrode showed excellent stability during 150 consecutive voltammetric cycles in 0.5 mol L^{-1} KCl solution as no decrease of the current was observed [4]. On the other hand, GF electrode was modified by a novel PB and ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF₄]) via simple method involving GF placed in a ultrasound bath of [Bmim][BF₄] and then in a PB precursor solution. In this case, the immobilization of [Bmim][BF₄] supported the anchoring PB nanoparticles on the surface of the GF [73].

Zeolitic Imidazolate Framework (ZIF-8) was recently proposed for modification of CF electrode from Atomic Layer Deposition of Zinc Oxide (ZnO) and its subsequent solvothermal conversion to ZIF-8. After heat treatments under control atmosphere, ZIF-8 conversion leads to microporous carbon structure with enhanced textural and electrochemical properties. The specific surface area of the CF was increased from 0.0915 to $64 \text{ m}^2 \text{ g}^{-1}$ for pristine and modified CF, respectively [74]. To give an overview of the modification methods (Fig. 3), Table 2 summarizes advantages and drawbacks of each one.

4 Carbon Felt-Based Material for Wastewater Treatment by EF Process

4.1 Carbon Felt for EF Process

CF are abundantly used for electrochemical applications and especially for EF process because of their outstanding properties like (1) high specific surface area and high efficiency for both hydrogen peroxide production and cathodic regeneration of Fe^{2+} , good mechanical integrity, and commercial availability, which make them an attractive cathode material for EF process [23, 76]; (2) good adaptability to various EF systems with different shapes and surfaces of electrodes from small (2 cm^2) [28, 77] to large size like 60 cm^2 [78, 79] or 150 cm^2 [80]; and (3) high physicochemical stability allowing a significant decline in the cost for the EF technology, since it can be continuously used for many cycles (at least ten cycles) without any decrease of the treatment efficiency [81].

The application of EF technology for elimination of POPs on CF cathodes has been preceded very early by Oturan and coworkers [82–84]. One of their first papers in 2000s described the EF process in a divided cell allowing almost total

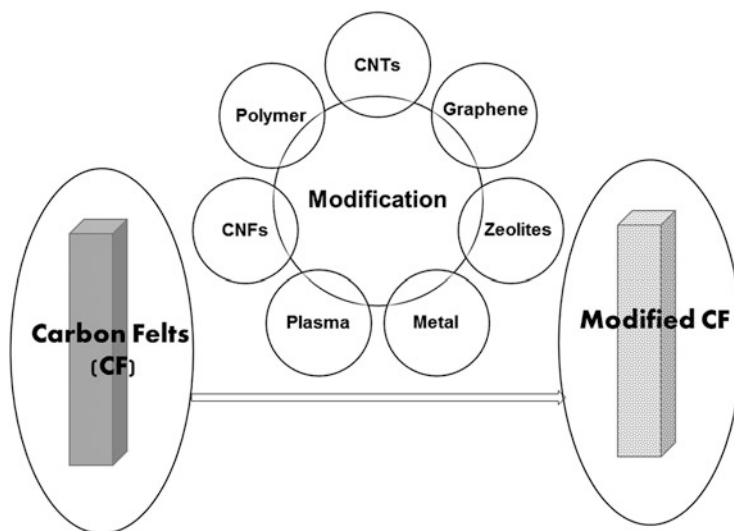


Fig. 3 The schematic for the modification processes of CF

mineralization (>95% total organic carbon (TOC) decay) of 1 mM phenoxyacetic herbicide 2,4-D after consuming 2,000 C [82]. Afterward, they continued developing their research using undivided cells combining CF cathode and Pt anode for the degradation of the herbicide diuron. A very high efficiency of 93% TOC removal at 1,000 C for 125 mL solution containing 40 mg L⁻¹ diuron has been reported [84]. From that, a series of studies using EF technology for water treatment on felt cathodes have been conducted to eliminate many different kinds of POPs in aqueous medium, including:

1. Dye pollutants: 95% TOC of the anthraquinone dye Alizarin Red S was removed in 210 min of electrolysis on GF (*Carbone-Lorraine*, thickness 0.5 cm)/boron-doped diamond (BOD) [85]. A mixture containing four triphenylmethane dyes, namely malachite green, crystal violet, methyl green, and fast green, with initial Chemical Oxygen Demand (COD) ca. 1,000 mg L⁻¹, was totally depolluted with efficiency near 100% at the beginning of the treatment on CF (*Carbone-Lorraine*) [86]. Other dyes were also investigated like malachite green [86], direct orange 61 (DO 61) [78], and acid orange 7 (AO7) [81, 87, 88].
2. Phenolic type compounds: 100% of TOC of aqueous phenol solutions was eliminated by EF process using CF cathode [89]. After 360 min of electrolysis, 95% TOC of the p-coumaric acid (4-hydroxycinnamic acid) was removed on GF (*Carbone-Lorraine*, thick 0.5 cm)/Ti-RuO₂ [90]. Pentachlorophenol [83, 91] and Bisphenol A [92] are also in this group.
3. Pesticides: the EF treatment has also been successfully applied to mineralize the herbicides and pesticides such as chlortoluron [79], 4-chloro-2-methylphenol (PCOC) [93], chlorophenoxy acid [82, 94, 95], and methyl parathion [96].

Table 2 The various modifications of carbon felt electrodes, advantages, and drawbacks of the method

Modification method	Electrode	Surface area increase	Conductivity increase	Stability	Advantages	Drawbacks	Reference
Chemical treatment	CF (SSGL Carbon, Germany)	–	2.5 times ^a	–	Relative low cost	Use of chemicals potentially toxic and not easy to handle	[18]
	GF (Shanghai Energy Carbon Limited Co., China)	1.5 times	–	Energy efficiency (EC) of vanadium redox flow battery (VRFE) above 77% after 20 cycles			[15]
Thermal treatment	CF (<i>Nippon Chem</i>)	1,344%	7% ^b	EC maintained of 75% after 500 cycles	Easy process	High energetically cost, require specific equipment	[5]
Graphene	GF (RVG-2000, Carbon-Lorraine)	–	12.5% ^b	EC maintained of 95% after 20 cycles	Very high efficiency	Stability unknown for long period of use	[37]
	CF	–	2% ^b	EC maintained of 93% after 30 cycles		Task of toxicity due to leaching of CNTs and graphene	[75]
Polymer	CF	–	300% ^a	–	Conductive polymer: high conductivity at room temperature and high stability	Stability unknown for long period of use	[56]
Zeolites	GF (Human Jiuhua Carbon Hi-Tech Co., Ltd., China)	2 times	<2 times ^c	–	Possibility to design different kind of zeolites with surface area	High cost	[62]

– Not determined

^aIncrease of the power density in MFC to raw CF^bIncrease of EC in VRFE to raw CF^cIncrease of the resistance of the electrodes to raw CF

4. Pharmaceuticals: Chlorophene [97], triclosan, and triclocarban [97] were examples for pharmaceutical pollutants which have been degraded efficiently by EF process using felt materials.
5. Hydrocarbons and polycyclic aromatic hydrocarbons (PAHs): EF process was also proposed to enhance the efficiency of soil washing treatment [80, 98, 99].

By the EF process, the pollutants are degraded step by step and eventually mineralized by reacting with hydroxyl radicals. The attack of hydroxyl radicals gives the formation of aromatic intermediate compounds at the beginning of electrolysis. The aromatic ring opening reactions in the next step create aliphatic carboxylic acids (oxalic, acetic, formic acid, etc.) and inorganic ions (i.e., ammonium, nitrate, sulfate, phosphate) as final end products before mineralization [97, 100–102]. Therefore, the EF mineralization also leads to the detoxification of treated solution [88, 91]. In particular, the toxicity of solutions disappeared after 240 min for 220 mL solution with 0.2 mM of sucralose [103], and 60 min for 200 mL solution with 50 mg L⁻¹ of Orange II [100]. The above results allow proposing EF process on CF cathode as an environmentally friendly method for the treatment of wastewater effluents containing toxic and/or persistent organic pollutants. Interestingly, more and more studies are focused now on CF modifications for improving EF processes as described in the following section.

4.2 Modified EF Systems Using Carbon Felt Cathodes

4.2.1 Modified Felt Cathodes for Homogeneous EF

For homogeneous EF process, hydrogen peroxide production and its reaction with catalyst in solution is a crucial factor for the effective destruction of POPs. Aiming to improve the in situ generation of H₂O₂, various attempts have been made to upgrade the electrocatalytic characteristic of CF cathodes. As discussed in Sect. 3.1, chemical modification is a simple and efficient way to ameliorate the electrochemical activity of the felt electrodes by changing their surface functional groups. After treatment in a mixture composed of ethanol and hydrazine hydrate (volume ratio 90/10), the concentration of H₂O₂ after 120 min was 175.8 mg L⁻¹ on the modified felt (CF-B) (*Shang-hai Qijie Carbon material Co., Ltd.*) which was nearly three times higher than 67.5 mg L⁻¹ for commercial CF. The p-nitrophenol TOC removal ratios were then 22.2% and 51.4% for CF and CF-B, respectively, proving that the treated cathode could efficiently promote the degradation efficiency of the pollutants with interesting stability and reusability (after ten cycles, the mineralization ratio was still above 45%) [23]. Anthraquinone-2,6-disulfonate/polypyrrole (AQDS/PPy) composite film was grown on graphite electrodes by electropolymerization of the pyrrole monomer in the presence of anthraquinone-2,6-disulfonic acid. Positive shifts (−0.65, −0.60, and −0.52 V vs SCE for pH 3.0, 4.0, and 6.0, respectively) were recorded indicating a better kinetics for oxygen

Table 3 Mineralization efficiency of homogeneous EF process applying diverse CF cathodes

Cathode material	Pollutant	% TOC removal increase ^a	% TOC removal decrease ^b	Reference
Graphene/CF	AO7	33	6	[77]
Chemically modified CF	p-nitrophenol	29	5	[108]
Thermally treated CF	Paracetamol	31	1	[105]

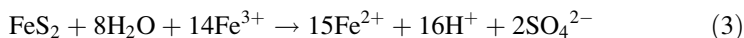
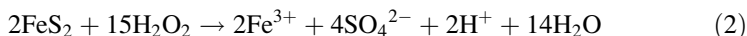
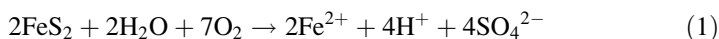
^aCompared to raw cathode after 2 h treatment

^bAfter five cycles

reduction compared to the bare cathode (-0.85 , -0.82 , and -0.77 V vs SCE for pH 3.0, 4.0, and 6.0, respectively), which indicated a better electrocatalytic activity of the AQDS/PPy/GF cathode toward oxygen reduction reaction (ORR). Therefore, the modified cathode resulted in a large accumulation of electrogenerated H_2O_2 which increases the EF degradation of amaranth azo dye [52]. Additionally, the improvement of the H_2O_2 formation rate was found on felt cathode modified by graphene using electrochemical deposition [77, 104], by heat treatment in a tubular furnace, by feeding by a mixture of N_2/O_2 with 1% of oxygen [105], by MWCNTs using the electrodeposition method carried out by applying the voltage of 17.5 V to the solution containing 0.3 g L^{-1} MWCNTs and 0.2 g L^{-1} CTAB [106], and by chemical treatment by electrochemical oxidization which was cyclically polarized in different concentration of H_2SO_4 solution in the range of 0.0 V to +2.0 V at a rate of 10 mV s^{-1} [107] (Table 3).

4.2.2 Modified Felt Cathodes for Heterogeneous EF

Drawbacks of Fenton's reaction are (1) the pH regulation between 2 and 4, (2) the loss of soluble iron catalyst [109, 110], and (3) the post-treatment requirements prior to discharge [111]. Heterogeneous catalyst could overcome these drawbacks. The main advantages of using solid iron sources are self-regulation and electrochemical regeneration of iron [112]. Pyrite is a low-cost and abundant natural iron sulfur mineral, which can provide iron ions and then act as a homogeneous catalyst after its dissolution. It seems to be a good candidate because when used as a suspension in the medium, it self-regulated the Fe^{2+} content and the pH in the solution in the presence of dissolved O_2 through reactions (1)–(3) [113]. Interestingly, the usage of pyrite can be repeated many times by the filtration to collect it from the solution. Therefore, pyrite has been used widely to remove many biorefractory pollutants in aqueous medium such as azo dye – the (4-amino-3-hydroxy-2-p-tolylazo-naphthalene-1-sulfonic acid) (AHPS) on GF (*Carbone Lorraine*, thickness 0.5 cm) [114], antibiotic levofloxacin [113], and tyrosol [113] on CF (*Carbone Lorraine*), etc.



Iron alginate gel beads (FeAB) were also used in suspension as heterogeneous catalyst in the EF treatment in which high imidacloprid removal (90%) was achieved using GF cathode (*Carbon Lorraine, France*) for 4 h [115]. Decolorization of Lissamine Green B and Azure B was 87% and 98%, respectively, after 30 min by using FeAB, maintaining particle shapes throughout the oxidation process [116].

Besides operating with solid catalyst in suspension, in 2017, Özcan et al. [117] prepared a new iron containing Fe_2O_3 -modified kaolin (Fe_2O_3 -KLN) catalyst to develop a heterogeneous EF process with three-dimensional CF cathode for the electrochemical oxidation of enoxacin (ENXN). In the presence of Fe_2O_3 -KLN, mineralization efficiency is increasing and the maximal value was found in the presence of 0.3 g catalyst at 300 mA with a very low iron quantity (~ 0.006 mM) leached in solution, showing that hydroxyl radicals were mainly produced by heterogeneous reactions of surface iron species immobilized on CF [117]. The durability of the catalyst was tested on five runs and a small decrease of around 0.5% was monitored [117]. EF treatment with heterogeneous pyrrhotite catalyst has also shown good stability with a stable color and COD removal of 77% and 78%, respectively, after 45 days. [118]. On the other hand, investigation on hierarchical CoFe-layered double hydroxide (LDH)-modified carbon felt cathode indicated that TOC removal declined 46% compared to fresh electrode after ten cycles, proving that stability has to be improved for this electrode [119].

The performance of the heterogeneous catalysis for the removal of pollutants by EF was also improved compared with homogeneous one. For example, a measured pseudo-first-order rate constant of $2.5 \times 10^{-4} \text{ s}^{-1}$ ($R^2 = 0.990$) was found for EF using pyrite catalyst which was nearly two times higher than the constant determined in electrochemical oxidation ($1.3 \times 10^{-4} \text{ s}^{-1}$ ($R^2 = 0.992$)). In addition, Fe@ Fe_2O_3 [120–122], pyrrhotite [118] γ -FeOOH [123, 124], and (γ - $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ oxides) nanoparticles [125] and chalcopyrite [126] are interesting iron catalyst sources. The stable performance of these heterogeneous iron catalysts open promising perspectives for fast and economical treatment of wastewater polluted by POP contaminants using EF treatment on CF cathodes. In a very recent study, one new kind of heterogeneous catalyst, hierarchical CoFe-Layered Double Hydroxide (CoFe-LDH), was grown on CF by in situ solvothermal method. The CoFe-LDH/CF cathode showed very good stability when after seven cycles of degradation the TOC removal after 2 h was still above 60% [119] (Table 4).

Table 4 CF cathodes for heterogeneous EF process

Cathode	Catalyst/cathodes	Experimental conditions	EF efficiency	Reference
CF	CoFe-LDH	40 mg L ⁻¹ of acid orange 7 (AO7) at pH 3 using Pt mesh at 4.2 mA cm ⁻²	87% TOC removal after 2 h; and 97% after 8 h	[119]
GF (Carbon Lorraine, France)	Iron alginate gel beads (FeAB)	100 mg L ⁻¹ of imidacloprid using BDD anode at constant potential drop of 5 V	90% of imidacloprid removal after 4 h	[115]
CF (Beijing Sanye Carbon Co., Ltd., China)	Pyrrhotite	Real landfill leachate using anodic microbial respiration in MFC system with maximum power density of 4.2 W m ⁻³	77% of color and 78% of COD were removed after 45 days	[118]
CF	γ-FeOOH	Oxidation of arsenite by bio-electro-Fenton process in dual-chamber microbial fuel cell (MFC)	The apparent oxidation current efficiency was 73.1%	[123]
CF (MAST Carbon International Ltd., Great Britain)	γ-Fe ₂ O ₃ /Fe ₃ O ₄	16 μg L ⁻¹ of diclofenac (DCF), applied potential of 2 V using EF filter	The mineralization current efficiency (MCE) was >20%	[125]

4.2.3 Hybrid EF System Using Carbon Felt Cathodes

To boost the degradation efficiency and reduce the treatment cost, many attempts have been made to change the EF reactor. A novel vertical-flow EF reactor, composed of ten cell compartments, was designed to degrade tartrazine, a model azo dye. GF cathode (*Shanghai Qijie carbon material Co., Ltd*) was modified by ultrasonic immersion and coating method, combined with PbO₂/Ti mesh anode. By comparing with the single cell using the parallel-flow EF reactor, the new configuration showed a higher performance. The tartrazine with initial concentration of 100 mg L⁻¹ could reach near 100% degradation but with a TOC removal efficiency of 61.64% [127]. This result came from the reason that the mass transfer rate of the target pollutant molecules is accelerated and the contaminants can be well enriched at the surface in vertical-flow reactor [128].

Rosales et al. [129] fabricated an EF reactor with continuous bubble to treat the wastewater containing synthetic dyes. High decoloration percentages of pollutants were found. On the other hand, methyl orange (MO) degradation was carried in a hemisphere-shaped quartz reactor using dual rotating GF disks (*Shanghai Qijie Carbon Material Co., Ltd*) cathode to supply oxygen. An efficient production of H₂O₂ without oxygen aeration was attributed to the rotation of the cathodic disk, offering a potentially cost-effective EF method for degrading organic pollutants [130].

To further reduce the costs of electricity input, bio-electro-Fenton (BEF) system has been developed. This approach couples the EF process with MCF which

generates electricity directly from organic compounds. Zhang et al. [131] used GF at both cathode and anode without external power supply for bio-electrochemical degradation of paracetamol. In this process, a dual-chamber MFC reactor operated in the anode chamber to release bio-electrons by oxidizing biodegradable pollutants in low-strength real domestic wastewater. In the cathode chamber, $\bullet\text{OH}$ production is possible because the electrons coming from the anode will promote oxygen reduction into hydrogen peroxide and then conversion into radicals in the presence of iron as catalyst. The transfer of iron (III)/iron (II) ($\text{Fe}^{3+}/\text{Fe}^{2+}$) (sourced from $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ added directly) from cathode to anode chamber is avoided with the use of a Proton Exchange Membrane (PEM, 6.0 cm \times 5.5 cm cross-sectional area, *Nafion-117, DuPont, USA*) [131].

The BEF system has also been developed toward a clean treatment by using heterogeneous catalysis to avoid iron-soluble salts adding. Birjandi et al. [121] built up a BEF cell through the combination of anaerobic seed sludge as biocatalyst in an anode chamber and $\text{Fe}@\text{Fe}_2\text{O}_3/\text{graphite}$ as cathode (*Entegris, Inc. FCBLK-508305-00004, USA*). This cathode served simultaneously to produce peroxide and as the catalytic iron source. The medicinal herb wastewater degradation was attributed to bio-oxidation by microorganisms at anodic chamber and to the EF process at cathodic one [121]. This BEF system was also performed by Zhuang et al. [132] on CF (4.5 cm \times 4.5 cm, *Liaoyang, China*). The electricity generated by MFC to in situ generate H_2O_2 at a CF cathode for EF process was also investigated to remove p-nitrophenol by Zhu et al. [133]. A power density of 143 mW m^{-2} was generated by the MFC, and p-nitrophenol was completely degraded after 12 h. Similar systems were created to remove biorefractory contaminants in wastewater sources like acid orange 7 dye using CF (5 cm \times 3 cm \times 0.5 cm, *Xinka Co., Shanghai, China*) [134], 17β -estradiol and 17α -ethynyl-estradiol estrogens using $\text{Fe}@\text{Fe}_2\text{O}_3/\text{CF}$ (4.5 cm \times 4.5 cm, *Liaoyang, China*) [120], azo dye (Orange II) [124] using CF anode and CNTs (CNTs)/ γ - FeOOH composite cathode, arsenite (As(III)) using γ - FeOOH/CF (4.4 cm \times 4.4 cm \times 0.5 cm) [123], Rhodamine B using $\text{Fe}@\text{Fe}_2\text{O}_3/\text{carbon felt}$, landfill leachate using CF (5 mm thickness, *Beijing Sanye Carbon Co., Ltd., China*) anode, and pyrrhotite/graphite (5 \times 7 cm^2 , 5 mm thickness) (*grade G10, Hongfeng Carbon Co., Ltd., Shanghai, China*) cathode [122].

Moreover, using modified felts can improve significantly the efficiency of BEF system. The BEF with the modified electrodes, PPy/AQDS-CF (5.0 cm \times 5.0 cm \times 0.6 cm, *Liaoyang Jingu Carbon Fiber Sci-Tech Co., Ltd., China*), resulted in the largest rate of H_2O_2 generation, beneficial for the enhancement in the amount of hydroxyl radicals produced and then the decolorization and mineralization of Orange II at neutral pH [54]. In order to avoid the use of expensive membranes in two-chamber microbial fuel cell (MFC) and to increase the generated power densities, more efficient dual reactor systems were advanced by using a single chamber in a modified electro-Fenton/MFC system. The power source from MFC was transferred directly to EF reactors constituted by CF cathode and iron plate anode as catalyst source. The TOC removal of phenol reached $75 \pm 2\%$ in the EF reactor in one cycle after 22 h treatment [135].

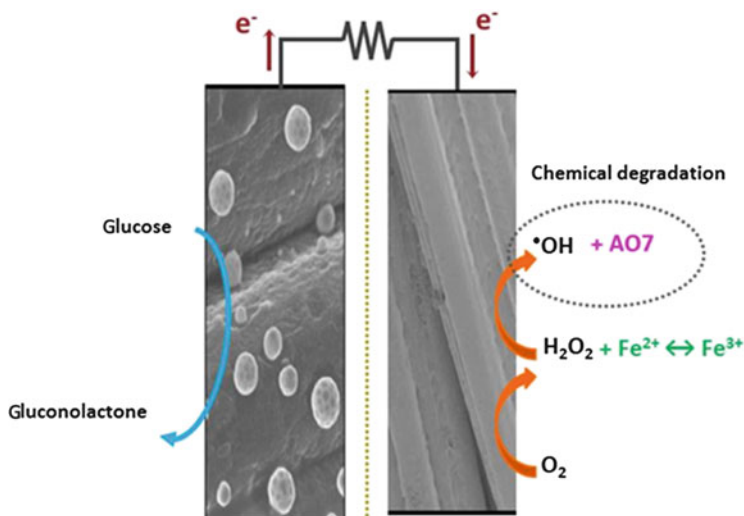


Fig. 4 Schematic diagram of the Fuel Cell-Fenton system. Reprinted from Le et al. [74]. Copyright (2016), with permission from ACS

Very recently, we discussed a Fuel Cell-Fenton system (Fig. 4) to degrade AO7 in a cell powered by abiotic oxidation of glucose. The cathode (CF/porous Carbon) was supplied by electrical energy of glucose oxidation at a CF electrode modified with gold nanoparticles. The cathode was fabricated by Atomic Layer Deposition (ALD) of ZnO on commercial CF followed by the solvothermal conversion of the metal oxide to a Metal Organic Framework (here ZIF-8). The as-prepared composite material further calcined at high temperature under controlled atmosphere of the material leads to microporous nitrogen-doped carbon. The average power output of the system was 170 mW m^{-2} , and a stability study was carried out for more than 2 months [74].

4.2.4 Industrial Applications

To assess industrial applications, the EF process was set up to treat large volume of contaminated solutions. An organic micropollutant, diclofenac (DCF), was removed from drinking water by a novel EF filter pilot working in continuous flow. The CF was used as material for both anode and cathode. The cathode was fabricated from iron nanoparticles ($\gamma\text{-Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ oxides) playing the role of catalyst. Because of CF electrodes high adsorption capacity of DCF, the protocol consisted of a first adsorption step without polarization for CF saturation followed by electrochemical degradation induced by an electrolysis step at 2 V inducing H_2O_2 production for EF process. Multiple cycles of adsorption/oxidation of DCF solutions were investigated at room temperature. In this EF pilot scale, the feed tank

contained 200 L. Satisfactory stability regarding both electrode integrity (no iron leaching) and removal efficiency was attained after multiple filtration/oxidation treatment cycles. The degradation of DCF and TOC removal was steadily achieved 85% and 36%, respectively, showing that efforts should be made to increase mineralization [125].

Sustainable energy sources were also investigated to supply power. There are some recent solar Photo-electro-Fenton (SPEF) systems as interesting examples: A volume of 8.0 L of textile dye solution, acid yellow 42, was treated efficiently by the SPEF process in a lab-scale pilot plant which decreased the energy consumptions [136]. The usage of sunlight as power source was also found in an autonomous solar pre-pilot plant with a capacity of 10 L to mineralize Yellow 4 diazo dye. At 5 A, about 96–97% mineralization was rapidly attained, and a reaction pathway for Direct Yellow 4 was proposed [137]. This solar pre-pilot plant also contributed to mineralize 89% of the antibiotic chloramphenicol [138], or 94% of sulfanilamide [139]. Electrode materials employed in this SPEF process were a boron-doped diamond anode and an air-diffusion cathode. Although this pilot did not use CF electrodes, this system was discussed here as an example of future development for EF pilot scale using sustainable energy sources.

5 Conclusion

Thanks to excellent properties with respect to electronic conductivity, chemical stability, light weight, and low cost, CF is widely applied as electrodes in energy and environmental field, especially water treatment by electrochemical methods. However, for application in aqueous medium, the high hydrophobicity of carbon makes it difficult to apply as electrodes. To overcome this drawback, modification methods can be used resulting in new and various benefits. Plasma, thermal, and chemical treatments change the hydrophobic surface of pristine felts to hydrophilic. They are easy to process but can suffer sometimes of a too high energy cost. Carbon nanotubes and graphene modification improved significantly the conductivity and the electrochemical active surface area; they present a risk of toxicity due to leaching in solution. Besides these modifications, zeolite material modification was also discussed.

Carbon-based modified material is a cheap, non-toxic, and stable cathode for wastewater treatment by EF process. Many toxic biorefractory pollutants were efficiently eliminated in short electrolysis time because of the significant improvement of hydrogen peroxide production, an important issue of EF process. On the other hand, to overcome the disadvantages of soluble catalyst, other solid iron sources were successfully applied for heterogeneous EF process. For industrial applications, new configurations like vertical-flow EF reactor stacked with ten cell compartments and continuous bubble EF process continually improved the efficiency of the treatment. The consumption cost was also considered by zero-energy EF approaches where MFC or abiotic fuel cells supplied clean power. These

hybrid EF systems are cost-effective for recalcitrant contaminants treatment, opening up new development trend for future research in the environmental and energy-related field. Sustainable approach using solar energy with air-diffusion cathodes for EF pre-pilot plants is also an interesting route for the future.

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