



Short communication

# Rhodium-catalyzed electrochemical hydrodefluorination: A mild approach for the degradation of fluoroaromatic pollutants



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## ABSTRACT

Many fluoroorganic compounds are toxic and persistent, and achieving their efficient degradation under mild conditions is currently a challenge. Herein, we developed a new electrochemical hydrodefluorination (HDF) system based on rhodium electrocatalyst for the degradation of fluoroaromatic (FA) pollutants. The HDF system realized the rapid degradation of 18 representative FAs to form nonfluorinated organics and  $F^-$  under mild conditions (room temperature and pressure, water medium, air atmosphere, without the use of hazardous reagents). This study may provide a new promising alternative for the practical treatment of waste water containing FA pollutants.

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## 1. Introduction

Fluoroorganic compounds (FOCs) are becoming widespread environmental pollutants because of their wide and increasing applications [1–12]. Many of these compounds are particularly persistent in the environment [4–6]; they are strongly resistant to traditional biological degradation [7,8] and conventional chemical processes [9,10] because of the inertness of C–F bond. The compounds gradually accumulate in the environment, achieving concentrations that are hazardous to living organisms [11,12].

Hydrodefluorination (HDF) is one of the most facile approaches to dispose of FOC pollutants [4]. The process simply transforms the C–F bond of FOCs to C–H, which could then dramatically increase the compounds' biodegradability. Numerous efficient HDF methods have been developed for FOC degradation. Among these approaches are the Lewis acid mediated [13,14], homogeneous [15–17] or heterogeneous [18,19] transition metal-catalyzed, and photo-reductive [20–22] HDF processes. Unfortunately, these HDF methods require harsh reaction conditions such as high temperature [15], high pressure [16], inert atmosphere [20–22], or using toxic hazardous reagents, such as the explosive hydrogen gas [18,19] and toxic organic solvents [13,14,17]. The persistent need for these conditions hinders the wide practical application of the aforementioned HDF methods. Compared with the above-mentioned HDF methods, electrochemical HDF is intrinsically milder and more likely to be operated under mild condition. So far, only few electrochemical HDF cases have been reported and these

HDF examples do not remove the use of high pressure [23] or toxic organic solvents [24]. Therefore, the development of HDF systems under mild conditions would be a significant achievement to address emerging environmental problems from the increasing use of FOCs and their persistence in the environment.

In this communication, we presented a mild and robust electrochemical HDF system for the degradation of fluoroaromatic (FA) pollutants. To the best of our knowledge, this paper is the first to report an electrochemical HDF system that degrades FAs to form nonfluorinated organics and  $F^-$  under room temperature and pressure without resorting to the use of toxic organic solvents and inert gases.

## 2. Material and methods

All FAs and their HDF products with purities of 98%–99%, as well as  $RhCl_3$  hydrate (99.5%), were acquired from Aladdin Reagent Co., China. Ni foams (1.0 mm thickness), Cu foams (1.0 mm thickness), Ag mesh (open area 37%), and carbon felt (2.0 mm thickness) were obtained from Cells Electrochemistry Co., Ltd., China ([www.hzcell.com](http://www.hzcell.com)). Rh-modified nickel (Rh/Ni) foam, silver (Rh/Ag) mesh, and copper (Rh/Cu) foam, were prepared by a metallic replacement reaction (exposing to a 30 mL aqueous solution containing 1 M NaCl and 1.5 mM  $RhCl_3$  at pH 2 adjusted using HCl until the rose color of the  $RhCl_3$  solution disappeared). Rh-modified carbon felt (Rh/carbon felt) was prepared by electrodeposition (using a constant current of 2 mA in the same  $RhCl_3$  solution until the rose color disappeared). The abovementioned four Rh-modified materials have the same Rh loading of 0.77 mg/cm<sup>2</sup> (projected area), unless otherwise noted. The Rh/Ni foam exhibited the highest HDF activity among the four

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Rh-modified materials. Hence, its surface morphology and composition, as well as the  $\text{Rh}^{n+}/\text{Rh}^0$  ratio value of surface Rh were determined by SEM (Hitachi S-4700 II) equipped with EDS (Thermo NOANVANTAGE ESI) and XPS (KRATOS AXIS ULTRA DLD), respectively. As shown in Fig. 1, a uniform Rh film was formed on the surface of Ni foam. It implies that the above-mentioned metallic replacement reaction is applicable to the preparation of Rh/Ni foam.

A conventional two compartment glass or PTFE H-cell separated by a Nafion-117 membrane was used for electrochemical HDF experiments. The cathode was fabricated from a piece of Rh/Ni foam, Rh/Ag mesh, Rh/Cu foam, or Rh/carbon felt (projected area:  $2 \times 3 \text{ cm}^2$ ), whereas the anode was fashioned from a graphite sheet ( $2 \times 3 \text{ cm}^2$ ). 30 mL phosphate buffer solutions (20 mM) served as both the catholyte and the anolyte. Unless otherwise noted, the catholyte was stirred with a stirring velocity of 350 rpm during electrolysis. The concentrations of reactants and their products were determined by an Agilent 7890 A gas chromatograph (GC) and a Waters HPLC system, using standard calibration curves. The fluoride ion ( $\text{F}^-$ ) concentration was determined by a REX PHSJ-4F pH/mV meter combined with  $\text{F}^-$  selective electrode (REX PF-202-C).

The specific electric energy consumption (*SEEC*,  $\text{kW h m}^{-3}$  catholyte) of the HDF process was calculated from the following equation:

$$SEEC = \frac{I \times U \times t}{1000 \times V}$$

where  $I$  is the applied current (A),  $U$  is the average cell voltage (3 V),  $t$  is HDF time (h), and  $V$  is the volume of the catholyte ( $3 \times 10^{-5} \text{ m}^3$ ).

Unless otherwise noted, all of the above-mentioned experiments were performed under air atmosphere, at 25 °C.

### 3. Results and discussion

#### 3.1. Optimization of HDF conditions

The electrocatalyst and its support, as well as the catholyte pH used usually determine the reaction efficiency of electrochemical hydrodechlorinations [25–28]. Thus, these parameters of the presented HDF system were optimized primarily with 4-fluorophenol (4-FP) as the target compound. We first examined the pH effects, of which the results are listed in Table 1 (entries 1–3). At pH values of approximately 11 and 7, the HDF efficiencies were discouraging over a Rh/Ni foam cathode (Rh as the electrocatalyst and Ni foam as the support), whereas the HDF efficiency was inspiring at a pH of approximately 3 (4-FP was completely converted, and near 100%

**Table 1**

Optimization of the electrocatalytic HDF system with 4-fluorophenol (4-FP) as the target compound.

Entry	Cathodes	pH	Conv. (%)	Yield of $\text{F}^-$ (%)
1	Rh/Ni foam	10.8–11.1	5	3
2	Rh/Ni foam	6.8–7.2	6	4
3	Rh/Ni foam	2.7–3.2	100	98
4	Pt/Ni foam	2.7–3.2	58	56
5	Ir/Ni foam	2.7–3.2	17	13
6	Ru/Ni foam	2.7–3.2	10	4
7	Pd/Ni foam	2.7–3.2	4	2
8	Rh/Cu foam	2.7–3.2	7	4
9	Rh/Ag mesh	2.7–3.2	14	5
10	Rh/Carbon felt	2.7–3.2	4	3
11 <sup>a</sup>	Rh/Ni foam	2.7–3.2	54	51
12 <sup>b</sup>	Rh/Ni foam	2.7–3.2	52	50
13 <sup>c</sup>	Rh/Ni foam	2.7–3.2	54	51
14 <sup>d</sup>	Rh/Ni foam	2.7–3.2	100	98
15 <sup>e</sup>	Rh/Ni foam	2.7–3.2	100	103

Unless otherwise noted, 30 mL of a 20 mM phosphate buffer aqueous solution containing  $120 \mu\text{M}$  ( $\mu\text{mol L}^{-1}$ ) 4-FP served as the catholyte, the applied current for 90 min was 0.52 mA (i.e., 0.52 mA/90 min, the charge passed was 8 F: 8 mol of electrons per mol 4-FP), the area of the cathode used was  $2 \times 3 \text{ cm}^2$  and a glass cell was used.

<sup>a</sup> 0.52 mA/22.5 min.

<sup>b</sup> Air free ( $\text{N}_2$ ), 0.52 mA/22.5 min.

<sup>c</sup> 0.52 mA/22.5 min, using a PTFE cell.

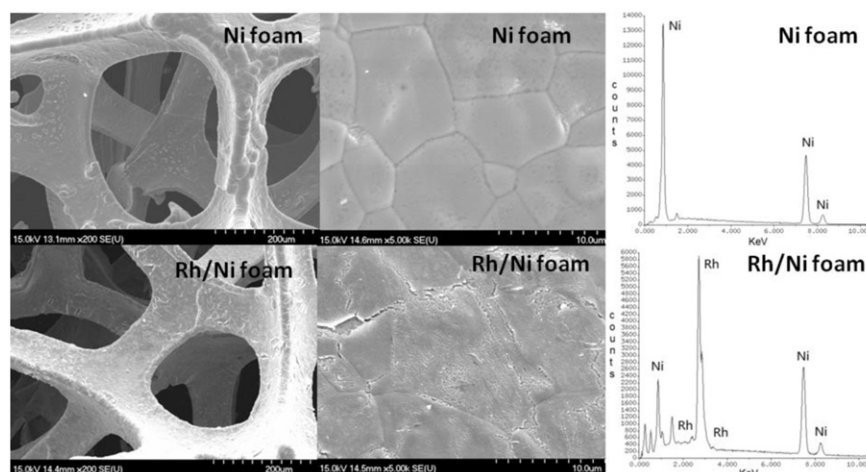
<sup>d</sup> 1.2 mM 4-FP, 5.2 mA/90 min.

<sup>e</sup> 12 mM 4-FP, 52 mA/90 min.

$\text{F}^-$  yield was achieved). We then examined the effects of the electrocatalyst and its cathode support. After screening different types of electrocatalysts (entries 3–7), such as Rh, Pt, Ir, Ru, and Pd, we determined that Pt exhibited the best performance as an HDF electrocatalyst besides Rh. Cathode support screening revealed that Ni foam provided a much higher yield of  $\text{F}^-$  compared with Cu foam, Ag mesh, and carbon felt (entries 3, 8–10). The higher HDF performance of the Rh/Ni foam probably was due to its small  $\text{Rh}^{n+}/\text{Rh}^0$  ratio value of 0.66 [29]. Aside from the above-mentioned three parameters, we also found that the HDF system is immune to air and the glass of the cell (entries 11–13) and that 4-FP at two higher concentrations degraded rapidly with 100% conversion and high  $\text{F}^-$  yield (entries 14 and 15).

#### 3.2. Degradation pathway of 4-fluorophenol and rate-limiting step

With the optimal HDF conditions in hand (water of pH 2.7–3.2 as the catholyte, Rh/Ni foam as the cathode), we evaluated the degradation pathway of 4-FP. 4-FP was reduced linearly to cyclohexanone (CYC.one) and cyclohexanol (CYC.ol) as the main organic products (Fig. 2A) with a



**Fig. 1.** SEM and EDS of the Ni foam and Rh/Ni foam.

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