



NASF SURFACE TECHNOLOGY WHITE PAPERS  
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8th Quarterly Report  
October-December 2022  
AESF Research Project #R-122

Electrochemical Approaches to Treatment of PFAS in Plating Wastewater

by  
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**Editor's Note:** For 2021, NASF-AESF Foundation Research Board has selected a project on addressing the problem of PFAS and related chemicals in plating wastewater streams. This report covers the eighth quarter of work (October-December 2022).

## 1. Introduction

This project started in January 2021 with the goal of developing applicable electrochemical approaches to remove per- and polyfluoroalkyl substances (PFASs) present in plating wastewaters, including electrooxidation (EO) and electrocoagulation (EC). This project includes three research tasks that are designed to investigate EC, EO and EC-EO treatment train, respectively, designed to probe three hypotheses specified follows:

- 1) EC generates amorphous metal hydroxide flocs that can effectively adsorb PFASs in plating wastewater, which, through an appropriate treatment, can release PFASs into a concentrated solution.
- 2) EO enabled by a Magnéli phase  $Ti_4O_7$  anode can be used to effectively destruct PFASs in plating wastewater.
- 3) The electrochemical treatment train comprised of EC and EO by  $Ti_4O_7$  anode can remove and degrade PFASs in plating wastewater more efficiently than either process operated individually.

Our previous report describes the results from experiments of EO with a Magnéli phase  $Ti_4O_7$  anode on the degradation of eight perfluoroalkyl acids (PFAAs), including perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorobutanesulfonic acid (PFBS), perfluorohexanesulfonic acid (PFHxS) and perfluorooctanesulfonic acid (PFOS). Here in this report, we describe a work to further explore how the degradation of different PFAAs are related to their molecular structures.

### 2.1 Chemical and reagent preparation

All chemicals used in the experiments were reagent grade and used as received. Polytetrafluoroethylene (PTFE) preparation (60 wt% dispersion in  $H_2O$ ) was obtained from Sigma Aldrich (St. Louis, USA). Sodium sulfate ( $Na_2SO_4$ ) and ammonium acetate ( $CH_3COONH_4$ ) were obtained from J.T. Baker Chemical (Phillipsburg, USA). Sodium perchlorate ( $NaClO_4$ ), sodium chloride ( $NaCl$ ) and HPLC-grade methanol were purchased from Fisher Scientific (Pittsburgh, USA). Sodium fluoride ( $NaF$ , 99%) was obtained from Alfa Aesar (Tewksbury, USA).

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### 2.2 Anodes Fabrication and Fluorination

In this experiment, Magnéli phase  $Ti_4O_7$  anodes were used, which were fabricated through high-temperature sintering and cut from one plate into smaller circular plates of the same size (2.2-cm diameter). The anodes were then surface fluorinated using an electrodeposition procedure in a reactive electrochemical membrane (REM) reactor.

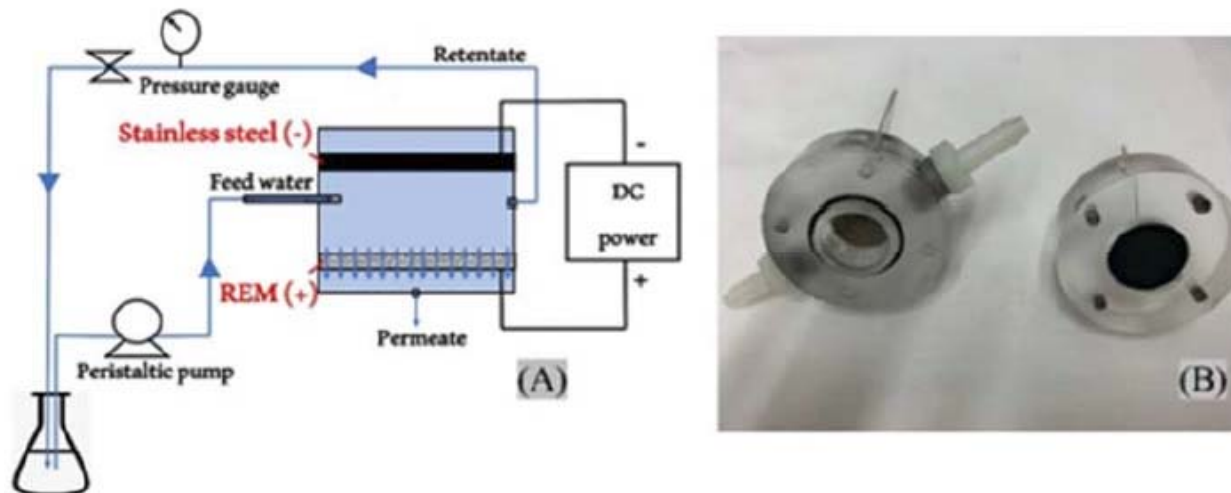


Figure 1 - (A) A schematic diagram of REM reactor with  $Ti_4O_7$  anode in cross-flow filtration operation; (B) a picture of actual reactor.

The reactor is shown in Figure 1. It consists of a cylindrical vessel with a  $Ti_4O_7$  anode and a circular stainless-steel cathode installed in parallel with a gap of 1.20 cm. There are inlet and outlet ports for the sample solution to flow through the space between the electrodes, and another outlet port is present on the anode side to collect the permeate. The retentate flow was recycled, while the permeate flow was not. The permeate flux was regulated by a back pressure regulator, and the flow rate was kept constant at 0.2 cm/min. Surface fluorination was performed in cross-flow mode, with a pristine  $Ti_4O_7$  plate as the anode. The feed solution contained 100-mM  $NaClO_4$  as the supporting electrolyte, and polytetrafluoroethylene (PTFE) resin at 0.5, 1.0, 2.0 or 5.0 mL/L, respectively with 10, 20, 30 or 40 mM of NaF. The pH of all deposition solutions was adjusted to 3.5. The REM operation was conducted for 60 min with a current density of 40 mA/cm<sup>2</sup> applied and the feed solution heated to 85°C in a water bath to facilitate electrodeposition of fluorine on the anode surface. The surface-fluorinated  $Ti_4O_7$  anodes were then stabilized at 150°C in a muffle furnace (KSL-1200X) (MTI Corporation, CA) overnight. Tests were conducted to confirm that no fluoride ion was released during electrooxidation in 100-mM  $Na_2SO_4$  solution at 20 mA/cm<sup>2</sup>.

### 3. Results and discussion

X-Ray photoelectron spectroscopy (XPS) was performed to examine the results of surface fluorination on the anodes performed by electrodeposition with solutions of varying NaF and PTFE concentrations (Table 1), and the spectra are displayed in Figure 2. Figure 2A presents the XPS full scan of pristine and fluorinated  $Ti_4O_7$  anodes. The oxygen O 1s, titanium Ti 2p and carbon C 1s peaks were observed at 532 eV, 461 eV and 287 eV, respectively, and their atomic percentages are listed in Table 2. The fluorine peaks were found around 687 eV on fluorinated  $Ti_4O_7$  anode surfaces, while it was absent on the pristine  $Ti_4O_7$  anode. A detailed scan of fluorine atom (Fig. 2B) exhibits a major peak at 689.5 eV, corresponding to the C-F bond in  $CF_3(-CF_2)_n$ , and a minor peak at 684.9 eV, corresponding to the Ti-F bond (Beamson and Briggs, 1992). This indicates that both the fluoroalkyl segments of PTFE and F<sup>-</sup> were electrodeposited on the  $Ti_4O_7$  surface, consistent with previous studies (Pei, *et al.*, 2021).

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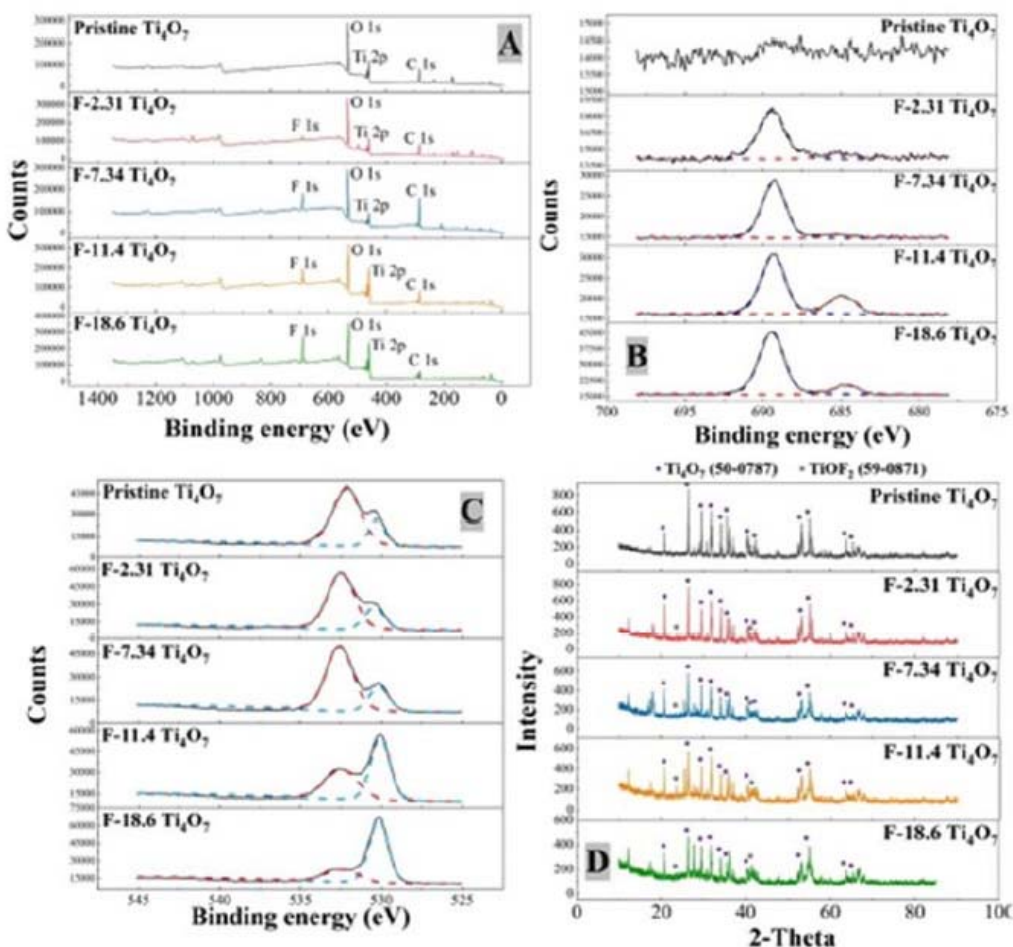


Figure 2 - The XPS analysis of pristine and surface fluorinated  $\text{Ti}_4\text{O}_7$  anodes: (A) XPS survey, (B) detailed scan of F 1s, (C) O 1s and (D) XRD results. The purple dots and grey dots represent the characteristic peaks of ICDD  $\text{Ti}_4\text{O}_7$  (50-0787) and  $\text{TiOF}_2$  (59-0871), respectively.

Based on the XPS data in Figure 2, the atomic percentages of F on  $\text{Ti}_4\text{O}_7$  anodes, respectively in Ti-F and C-F form and the total F, are summarized in Table 1. As seen in Table 1, the atomic percentages of F on the  $\text{Ti}_4\text{O}_7$  anodes were 2.31%, 7.34%, 11.4% and 18.6%, increasing along with the rising NaF and PTFE concentrations used in the electrodeposition solutions. The surface-fluorinated  $\text{Ti}_4\text{O}_7$  anodes are then named according to their respective F percentage, *i.e.*, F-2.31, F-7.34, F-11.4, or F-18.6  $\text{Ti}_4\text{O}_7$  (Table 1), respectively, from this point forward. Elemental mapping of F and C by EDS survey of the fluorinated  $\text{Ti}_4\text{O}_7$  anode surface confirms the existence of  $\text{CF}_3(-\text{CF}_2)_n$  groups (Figure 3).

Table 1 - The atomic percentage (%) of different elements on pristine and fluorinated  $\text{Ti}_4\text{O}_7$  anodes.

Name	Deposition solution		F 1s		
	NaF (mM)	PTFE ( $\text{mL}\cdot\text{L}^{-1}$ )	Total (%)	C-F (%)	Ti-F (%)
F-2.31 $\text{Ti}_4\text{O}_7$	10	0.5	2.31	2.00	0.31
F-7.34 $\text{Ti}_4\text{O}_7$	20	1.0	7.34	6.72	0.62
F-11.4 $\text{Ti}_4\text{O}_7$	30	2.0	11.4	8.43	2.97
F-18.6 $\text{Ti}_4\text{O}_7$	40	5.0	18.6	16.2	2.40

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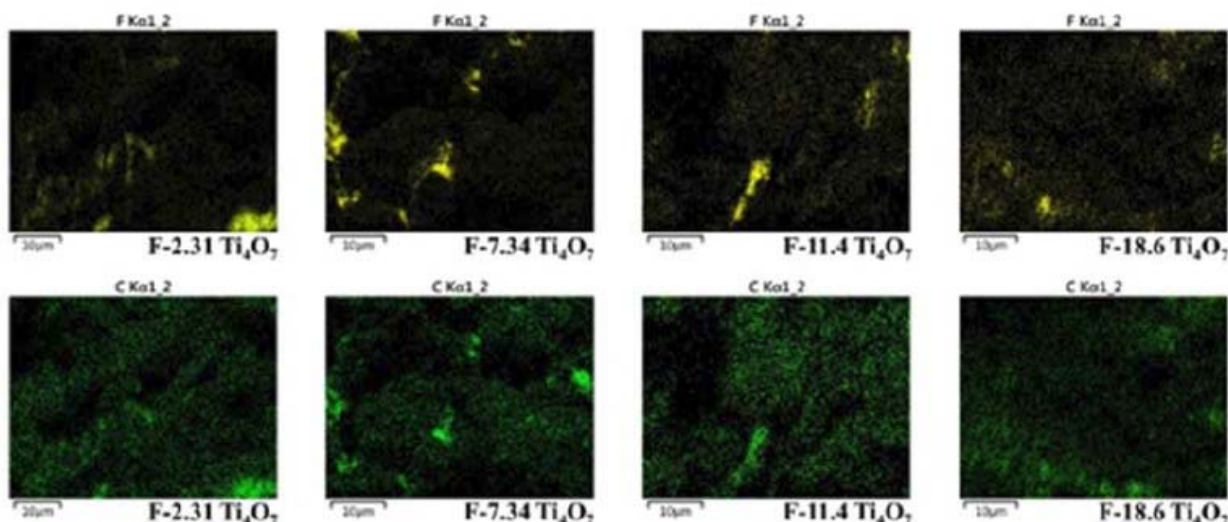


Figure 3 - The element mapping of fluorine (yellow) and carbon (green) on fluorinated  $Ti_4O_7$  anodes.

The data in Table 1 also suggests that the C-F form dominates in the surface-fluorinated surface instead of Ti-F. Moreover, it is noted that the increasing F atom percentage (from 2.31% to 18.6%) corresponds to a decreasing O atom percentage (from 53.3% to 36.6%) on the anode surfaces (Table 2), indicated by the O 1s peak of 532.5 eV binding energy (Fig. 2C). This suggests that surface fluorination of  $Ti_4O_7$  occurred by the substitution of -OH in the surface titanol group ( $\equiv TiOH$ ) by F and  $CF_3(-CF_2)_n$ .

XRD was performed to characterize the pristine and fluorinated  $Ti_4O_7$  anodes with standard reference materials to identify their compositions and phases (Fig. 2D). The XRD pattern of pristine and fluorinated  $Ti_4O_7$  anodes are similar, primarily composed of  $Ti_4O_7$ . The diffractive peak at  $2\theta = 21.5^\circ$  and  $41.3^\circ$  in fluorinated  $Ti_4O_7$  anodes indicates the appearance of  $TiOF_2$  in  $Ti_4O_7$  lattice.

Table 2 - Composition of electrodeposition solution and corresponding atomic concentration of F on the  $Ti_4O_7$  anode.

	F 1s			O 1s			Ti 2p	C 1s
	Total	C-F	Ti-F	Total	Ti-O	Surface -OH		
<b>Pristine <math>Ti_4O_7</math></b>	BDL			53.4	10.3	43.1	25.3	10.1
<b>F-2.31 <math>Ti_4O_7</math></b>	2.31	2.00	0.31	49.9	11.1	38.8	21.6	6.76
<b>F-7.34 <math>Ti_4O_7</math></b>	7.34	6.72	0.62	45.6	11.6	34.0	13.3	27.6
<b>F-11.4 <math>Ti_4O_7</math></b>	11.4	8.43	2.97	40.1	18.2	21.9	21.2	12.7
<b>F-18.6 <math>Ti_4O_7</math></b>	18.6	16.2	2.40	36.6	26.6	9.96	22.9	15.7

#### 4. References

1. G. Beamson and D.R. Briggs, *High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database*, J. Wiley & Sons, Chichester, UK, 1992.
2. S. Pei, H. Shi, J. Zhang, S. Wang, N. Ren and S. You, "Electrochemical removal of tetrabromobisphenol A by fluorine-doped titanium suboxide electrochemically reactive membrane," *Journal of Hazardous Materials*, **419**, 126434 (2021).

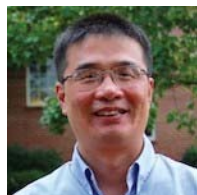


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### 5. Past project reports

1. Introduction to Project R-122: Summary: *NASF Report in Products Finishing, NASF Surface Technology White Papers*, 85 (6), 13 (March 2021); Full paper: <http://short.pfonline.com/NASF21Mar1>.
2. Quarter 1 (January-March 2021): Summary: *NASF Report in Products Finishing, NASF Surface Technology White Papers*, 85 (12), 13 (September 2021); Full paper: <http://short.pfonline.com/NASF21Sep1>.
3. Quarter 2 (April-June 2021): Summary: *NASF Report in Products Finishing, NASF Surface Technology White Papers*, 86 (3), 18 (December 2021); Full paper: <http://short.pfonline.com/NASF21Dec2>.
4. Quarter 3 (July-September 2021): Summary: *NASF Report in Products Finishing, NASF Surface Technology White Papers*, 86 (6), 16 (March 2022); Full paper: <http://short.pfonline.com/NASF22Mar2>.
5. Quarter 4 (October-December 2021): Summary: *NASF Report in Products Finishing, NASF Surface Technology White Papers*, 86 (9), 21 (June 2022); Full paper: <http://short.pfonline.com/NASF22Jun2>.
6. Quarter 5 (January-March 2022): Summary: *NASF Report in Products Finishing, NASF Surface Technology White Papers*, 86 (12), 22 (September 2022); Full paper: <http://short.pfonline.com/NASF22Sep2>.
7. Quarter 6 (April-June 2022): Summary: *NASF Report in Products Finishing, NASF Surface Technology White Papers*, 87 (3), 17 (December 2022); Full paper: <http://short.pfonline.com/NASF22Dec1>.
8. Quarter 7 (July-September 2022): Summary: *NASF Report in Products Finishing, NASF Surface Technology White Papers*, 87 (6), 19 (March 2023); Full paper: <http://short.pfonline.com/NASF23Mar2>.

### About the author



Qingguo (Jack) Huang is Professor in the Department of Crop and Soil Sciences, University of Georgia, Griffin Campus. He holds a B.S. in Environmental Science (1990) and a Ph.D. in Chemistry (1995) from Nanjing University, China as well as a Ph.D. in Environmental Engineering from the University of Michigan, Ann Arbor, Michigan. Dr. Huang's research interest focuses on catalysis involved in the environmental transformation of organic pollutants, and development of catalysis-based technology for pollution control and environmental remediation and management. His laboratory has been actively involved in several cutting-edge research topics:

- Enzyme-based technology for water/wastewater treatment and soil remediation
- Electrochemical and reactive electrochemical membrane processes in wastewater treatment
- Catalysis in biofuel production and agro-ecosystem management
- Environmental fate and destructive treatment methods of PFASs
- Environmental application and implication of nanomaterials

He has published over 170 peer-reviewed journal articles, five book chapters and four patents and three patents pending. He has taught three courses at the University Georgia: *Introduction to Water Quality*, *Environmental Measurement* and *Advanced Instrumental Analysis in Environmental Studies*.