

10th Quarterly Report
April-June 2023
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 tenth quarter of work (April-June 2023). A printable PDF version of this report is available by clicking **HERE**.

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 Ti₄O₇ anode can be used to effectively destruct PFASs in plating wastewater.
- 3) The electrochemical treatment train comprised of EC and EO by Ti₄O₇ anode can remove and degrade PFASs in plating wastewater more efficiently than either process operated individually.

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In our previous report, we described results on performance of surface fluorinated Ti_4O_7 anodes on PFAS degradation in batch mode. By comparing reaction rate constant and anodic potential in pristine Ti_4O_7 anodes and surface fluorinated Ti_4O_7 , we suggested the intrinsic reactivity of Ti_4O_7 anodes towards PFAS was reduced upon surface fluorination but compensated by the increase in anode effective electroactive surface area (EESA) from fluorination. In this quarterly report, we further examined the effect of surface fluorination of Ti_4O_7 anodes on PFAS degradation performance in terms of energy performance as well as formation of chlorate and perchlorate when chloride is present in the solution.

Tests and results

Based on the measured reaction rate constants from experiment illustrated in the last report, the electric energy required to reduce the concentration of target contaminant by one order of magnitude (EE/O) was calculated for each anode and plotted in Figure 1. For all anodes, it follows a general trend that the EE/O first decreases with increasing anodic potential because of rising reaction rates, but then increases as more energy is wasted on water oxidation at higher anodic potential. The optimal range of the anodic potential appears to be 3.2 to 3.6 V (vs SHE) regarding the lowest EE/O. Surface fluorination of the anodes slightly increased the EE/O. The EE/O at 10 mA·cm⁻² were 5.09, 5.55, 5.84, 6.02 and 6.24 kWh·m⁻³ for the pristine, F-2.31, F-7.34, F-11.4 and F-18.6 Ti_4O_7 anode, respectively.

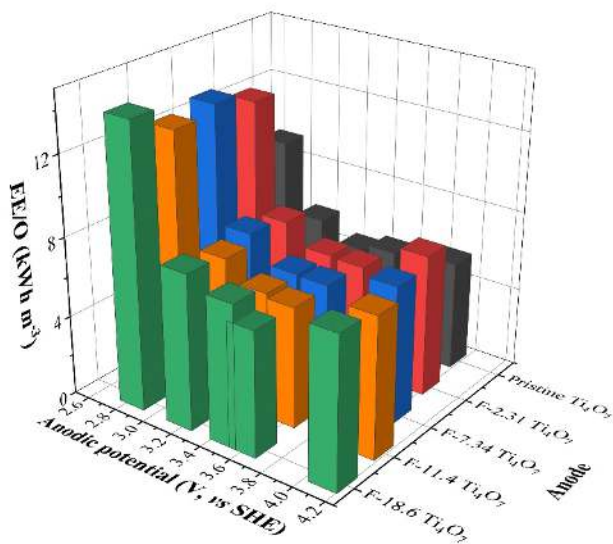


Figure 1. EE/O in relation to the anodic potential for PFASs degradation during EO treatment in batch mode on pristine and surface fluorinated Ti_4O_7 anodes. Initial PFAS concentration: 2 μ M, supporting electrolyte: 100-mM Na_2SO_4 + 10-mM $NaCl$.

After repeated EO experiment described above, XPS characterization was performed again on F-18.6 Ti_4O_7 anode and compared to that collected before the EO experiment in Figure 2 to verify the stability of the anode surface fluorination. As seen in Figure 2, the total atomic percentage of F increased from 18.6% to 20.31% after the EO experiments. The $CF_3(-CF_2)_n$ at binding energy 689.5 eV before and after EO experiments did not change significantly (16.2% to 16.4%), indicating its great stability on the anode,

while Ti-F at binding energy 684.9 eV increased from 2.40% to 3.91%. It may result from the fluorine released from PFOA, PFOS and 6:2 FTS mineralization during EO binding to Ti on the Ti_4O_7 anode¹.

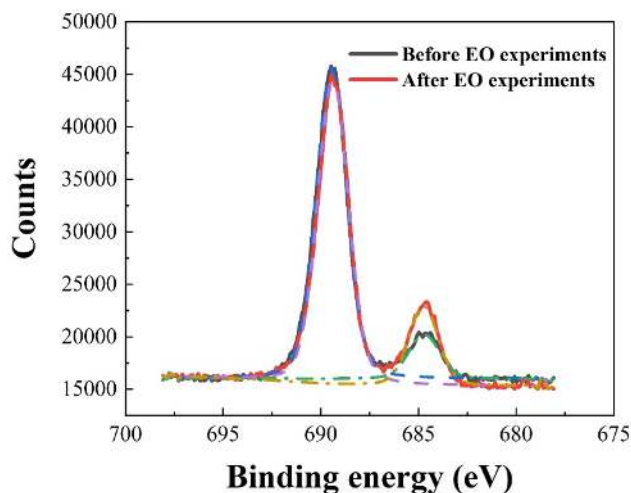


Figure 2. The F 1s scan of F-18.6 Ti_4O_7 anode before and after EO experiments.

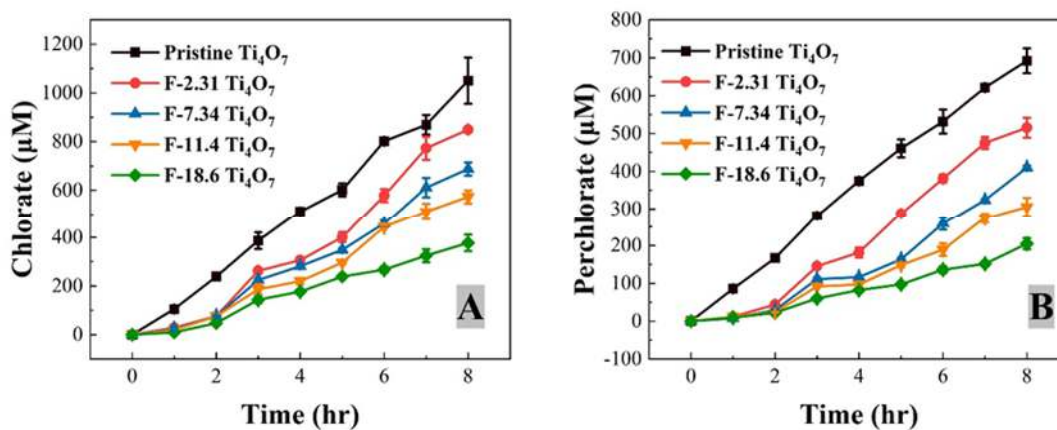


Figure 3. The formation of chlorate (A), perchlorate (B) during EO with pristine and fluorinated Ti_4O_7 anodes at $10\text{ mA}\cdot\text{cm}^{-2}$. The solution contained PFOA, PFOS and 6:2 FTS each at the initial concentration of $2.0\text{ }\mu\text{M}$. Supporting electrolyte: $100\text{-mM Na}_2\text{SO}_4 + 10\text{-mM NaCl}$. Error bar represents standard deviations of replicates.

Cl^- can be oxidized to chlorate and perchlorate ions through a series of reactions, including DET and $\cdot OH$ -mediated reactions during electrooxidation, initiated by the oxidation of Cl^- to form $Cl\cdot$ on the anode^{2,3}. Formation of chlorate and perchlorate was observed during the EO treatments of PFASs shown in previous reports, as the testing solutions contained 10-mM NaCl . Figure 3 displays the time-course profiles of the chlorate and perchlorate concentrations during the EO treatment at $10\text{ mA}\cdot\text{cm}^{-2}$ with pristine and fluorinated Ti_4O_7 anodes, and their concentrations at the end of 8-hrs EO treatment at

different anodic potentials are present in Figure 4. It is evident in both figures that the formation of chlorate and perchlorate decreased with increasing surface fluorination.

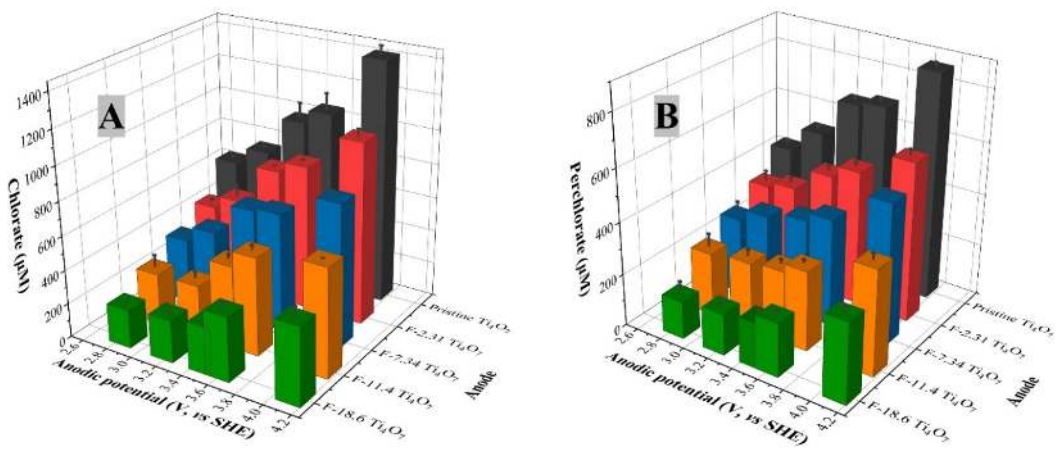


Figure 4. The concentration of chlorate (A) and perchlorate (B) at different anodic potentials on pristine and fluorinated Ti₄O₇ anode at 8-hour electrooxidation. Initial PFAS concentration: 2 µM, supporting electrolyte: 100-mM Na₂SO₄ + 10-mM NaCl. Error bar represents standard deviations of replicates.

References

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3. Donaghue, A., Chaplin, B.P., 2013. Effect of Select Organic Compounds on Perchlorate Formation at Boron-doped Diamond Film Anodes. *Environmental Science & Technology* 47, 12391-12399.

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), 11-14 (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), 5-8 (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), 5-9 (June 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), 1-4 (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), 9-11 (March 2023); Full paper: <http://short.pfonline.com/NASF23Mar2>.
9. Quarter 8 (October-December 2022): Summary: *NASF Report in Products Finishing; NASF Surface Technology White Papers*, **87** (9), 19 (June 2023); Full paper: <http://short.pfonline.com/NASF23Jun1>.
10. Quarter 9 (January-March 2023): Summary: *NASF Report in Products Finishing; NASF Surface Technology White Papers*, **87** (12), 12-15 (September 2023); Full paper: <http://short.pfonline.com/NASF23Sep2>.

About the author



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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 and five book chapters, and had five patents awarded 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.