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Electrochemical Oxidation of Seawater for Renewable Energy Generation and Storage in Coastal Areas

October 2024

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Abstract

In this work, we demonstrated how the Clean Sustainable Electrochemical Treatment process can be used to process seawater while simultaneously generating molecular hydrogen. The specific goal of this project is to (1) demonstrate selective removal of chemical oxygen demand over the oxygen and chlorine evolution reactions, (2) optimize electrode composition to improve electrochemical performance, and (3) demonstrate long-term (>100 h) stability experiments.

Summary

In this study, we investigated the Clean Sustainable Electrochemical Treatment (CleanSET) reactor's performance for processing seawater (SeaSET) containing biogenic organic compounds. We evaluated how the seawater composition, anode formulation, and electrochemical reaction conditions (i.e., voltage and current) affected the long-term stability, efficiency, and energy required to produce H_2 and remove chemical oxygen demand. We demonstrated that voltage and anode formulation affect SeaSET performance in both batch and continuous-flow experiments. We synthesized and tested different formulations of the ruthenium-based electrode and observed that they all improved the electrocatalytic activity by up to an order of magnitude. To better manage solid and gas generation, we also redesigned the continuous-flow electrolyzer. After long-term experiments, we observed that the anodes were damaged by pitting corrosion, erosion of active material, and passivation of the underlying titanium substrate.

Acknowledgments

This research was supported by the Strategic Investment Program under the Laboratory Directed Research and Development (LDRD) Program at Pacific Northwest National Laboratory (PNNL). PNNL is a multi-program national laboratory operated for the U.S. Department of Energy (DOE) by Battelle Memorial Institute under Contract No. DE-AC05-76RL01830.

Acronyms and Abbreviations

BOC	biogenic organic compounds
CE	current efficiency
CER	Cl2 evolution reaction
CleanSET	Clean Sustainable Electrochemical Treatment
COD	chemical oxygen demand
EDX	energy-dispersive X-ray spectroscopy
H2	hydrogen
OER	oxygen evolution reaction
RHE	reversible hydrogen electrode
Ru	ruthenium
SeaSET	Seawater Sustainable Electrochemical Treatment
SEM	scanning electron microscopy

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1.0 Introduction

In this work, we evaluated how the proprietary Clean Sustainable Electrochemical Treatment (CleanSET) technology performed for electrochemical oxidation of seawater (SeaSET) while simultaneously producing molecular hydrogen (H_2). The CleanSET technology was originally developed at Pacific Northwest National Laboratory to simultaneously oxidize and reduce biomass-derived streams; however, it has now been extended to process alkaline waters.[1] We demonstrated that biogenic organic compounds (BOCs) present in seawater can be selectively removed while simultaneously generating H_2 as a byproduct.

Currently, electrolyzing seawater is a challenging task due to the production of corrosive species such as chlorine (Cl_2) gas. Instead, our proposed technology targets the electrolysis of BOCs present in seawater to generate H_2, thus preventing Cl_2 generation.

The proposed feed-agnostic process takes advantage of electrochemical oxidation of organic compounds[2] and, as we have demonstrated, is more energy efficient for generating H_2 than (sea)water electrolysis. It also represents a novel way to electrify coastal communities. For example, our proprietary RuO_2-thin-film electrode selectively oxidizes the organic compounds present in wastewater (e.g., $CH_3COOH + 2H_2O \rightarrow 2CO_2 + 4H_2$, −0.02 V and 7.7 kWh/kg H_2) at lower energy requirements than the oxygen evolution reaction (OER: $2H_2O \rightarrow O_2 + 2H_2$, 1.23 V) or the Cl_2 evolution reaction (CER: $2Cl^- \rightarrow O_2 + H_2$, 1.38 V).[3-4]

2.0 Experimental Approach

We demonstrated the performance of the SeaSET process for removing chemical oxygen demand (COD) and simultaneously generating H_2 as a function of anode half-cell potential (1.0 to 3.0 V vs. reversible hydrogen electrode [RHE]) and anode formulation in batch and continuous-flow electrolyzers. The electrochemical performance—including half-cell potential, full cell potential, and current—was controlled and recorded by an AMETEK VersaSTAT 3 for the continuous-flow electrolyzer, as well as a Bio-Logic VMP-3e multichannel potentiostat. The gas products were analyzed with an INFICON Micro GC Fusion gas analyzer to determine H_2 and carbon dioxide production. The liquid phase was analyzed via high-performance liquid chromatography, liquid chromatography, inductively coupled plasma spectroscopy, and Hach analysis for COD and ammonia concentration.

Several anode formulations were synthesized via the sol-gel Pechini method, where the metallic precursor was deposited onto a titanium substrate via drop casting and heat treated to decompose the metal precursors. Ru-based anodes were assembled in a batch and continuous-flow cell and tested at ambient pressure and temperature for > 100 h in 0.6 M NaCl with and without 12,000 ppm COD from BOCs. The batch experiments were performed in an undivided redox.me 200 mL cell. However, the continuous-flow experiments were performed in a two-compartment SeaSET electrolyzer with a Nafion 117 membrane made in house. The performance of the various RuO_2-based anodes was compared against that of the baseline RuO_2 anode in terms of current density, current efficiency (CE), and energy required to remove COD or produce H_2.

3.0 Results and Discussion

3.1 Electrode and Condition Screening in Batch Cells

Figure 1 (a–d) summarizes the performance of the different Ru-based anodes and their impact on ECO performance (i.e., current density and specific current) at both 1.5 V and 2.0 V, versus a reversible H_2 electrode (RHE) in the presence and absence of BOCs in model seawater in 0.6 M NaCl. **Figure 1**(e) shows CE for COD removal from long-term experiments in 0.6 M NaCl with and without 12,000 ppm of COD from BOCs.

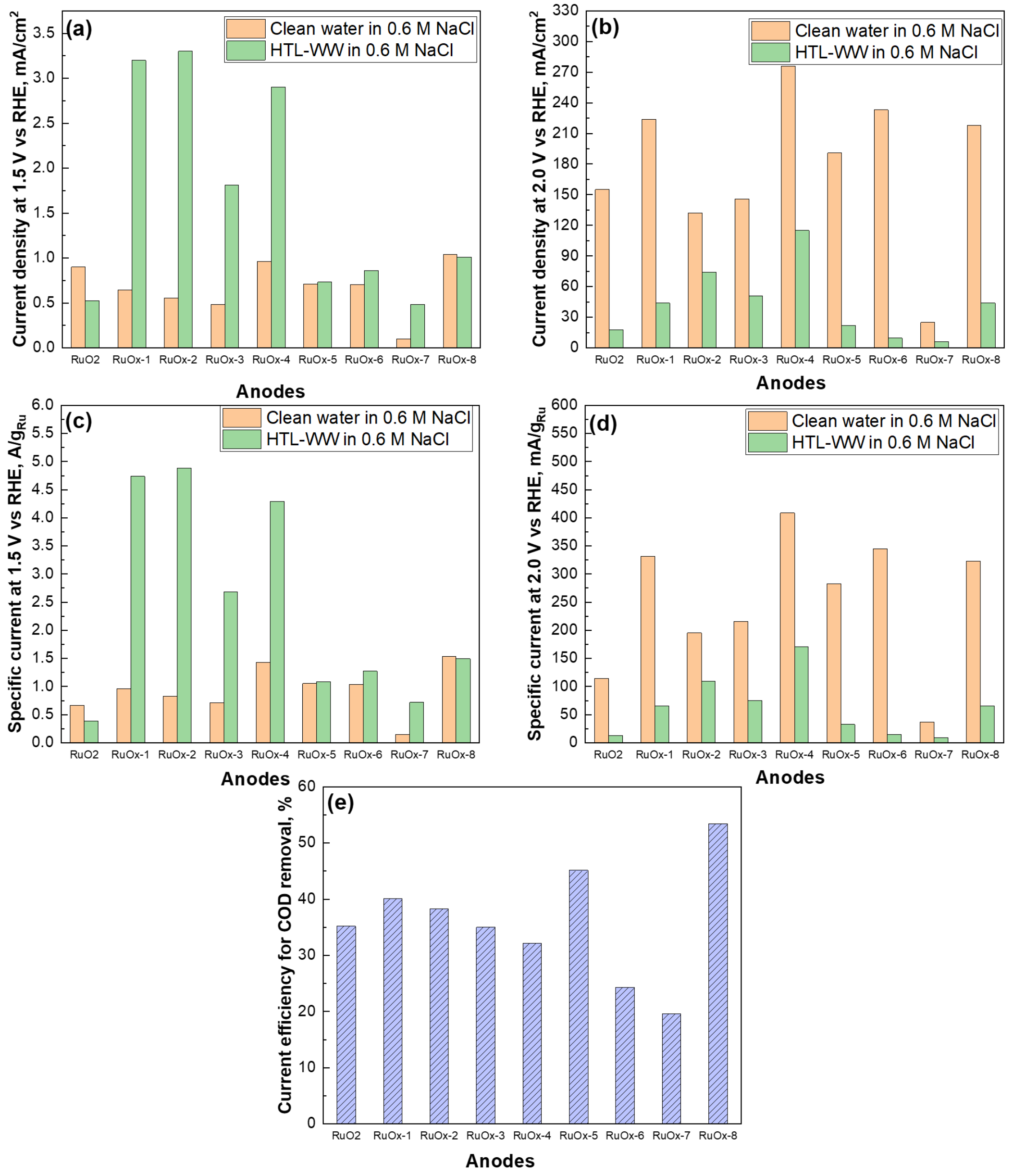
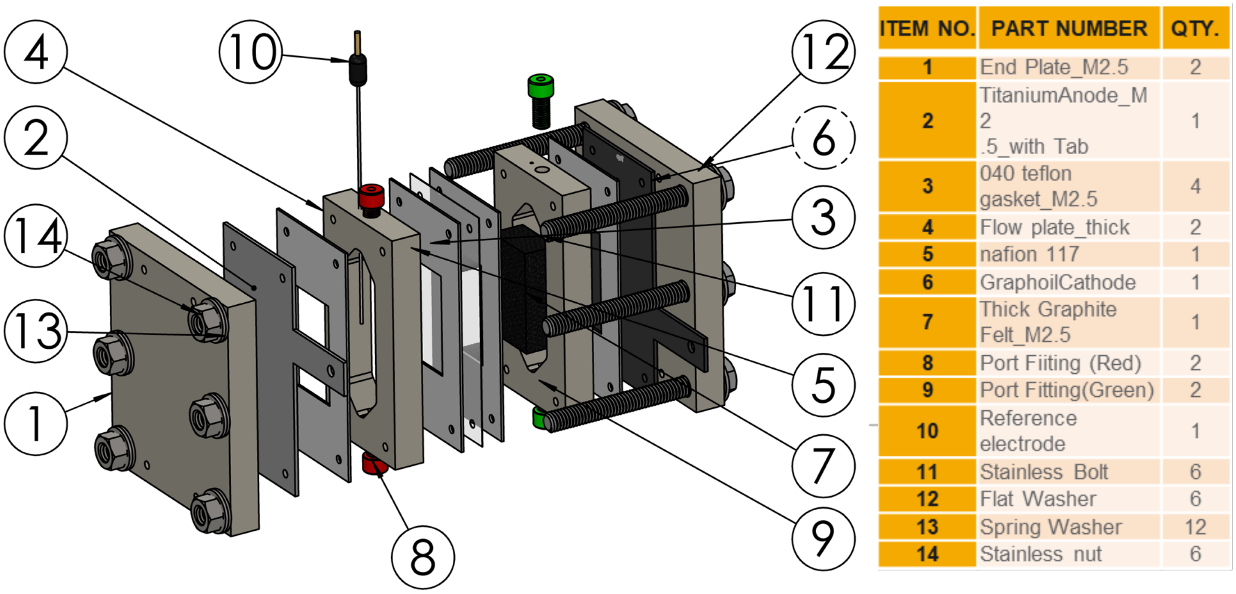


Figure 1. Electrochemical performance of Ru-based electrodes in 0.6 M NaCl with and without BOCs at 1.5 and 2.0 V vs. RHE. The activity is normalized as (a, b) current density (mA/cm^2), and (c, d) specific current (mA/g Ru). (e) CE for COD removal using different anodes in a 0.6 M NaCl system with 12,000 ppm of COD from BOCs.

The different anode formulations shown in **Figure 1** resulted in an increase in the current density (normalized by the cross-sectional area of the electrode) by up to a factor of 8 and in the specific current (normalized by the mass of Ru) by up to a factor of 13. The largest increases were observed at 1.5 V vs. RHE with the BOCs using RuOx-4, suggesting preferential removal of BOCs over OER and CER. However, all electrodes except RuOx-6 and RuOx-7 exhibited increased activity compared to RuO_2. The CE for COD removal for RuOx-8 was ≈1.5 times higher than that of RuO_2. All electrodes show similar or higher CE than RuO_2 except for RuOx-6 and RuOx-7. Future work will focus on further optimizing electrodes and electrolytes for operation at different reaction conditions and long-term experiments.

3.2 Flow SeaSET Electrolyzer Redesign



ITEM NO.	PART NUMBER	QTY.
1	End Plate_M2.5	2
2	TitaniumAnode_M2.5_with Tab	1
3	040 teflon gasket_M2.5	4
4	Flow plate_thick	2
5	nafion 117	1
6	GraphoilCathode	1
7	Thick Graphite Felt_M2.5	1
8	Port Fiiting (Red)	2
9	Port Fitting(Green)	2
10	Reference electrode	1
11	Stainless Bolt	6
12	Flat Washer	6
13	Spring Washer	12
14	Stainless nut	6

Figure 2. Schematic of the improved SeaSET electrolyzer design showing the different components, construction material, and assembly.

The original CleanSET electrolyzer design used microchannel flow plates that were hydraulically connected via a manifold that added two (inlet and outlet) 90° bends to the flow path. The combination of small channels and sharp bend angles made the design prone to over pressurization and clogging when precipitates and gas bubbles formed during the experiment. Thus, we increased the depth of the hydraulic flow path and removed the 90° bends by directly drilling the liquid inlets into the flow plate (**Figure 2**). The simplified SeaSET design diminished the chances of precipitates clogging the cells and helped with managing the gaseous products formed during electrolysis (i.e., H_2, O_2, and CO_2).

Electrolysis in a chlor-alkali medium created sodium hydroxide and hydrochloric acid as byproducts, which coupled with the already alkaline seawater media led to dissolution of iron (as iron hydroxide) from the stainless-steel fittings and pump head. The iron hydroxide precipitant successfully exited the cell but clogged the magnetic pump heads. Thus, we used diaphragm pumps constructed entirely of inert materials to prevent leaching of metal ions. Initial testing of the new pumps was successful (**Figure 3**) because they provided trouble-free fluid flow at stable flow rates without any precipitate formation.

3.3 Electrode and Conditions Testing in Flow Cell

The performance of RuO_2 and RuOx-5 anodes was tested at 2.2 V vs. RHE in 0.6 M NaCl with and without 12,000 ppm of COD from BOC to study the stability, CE, and the energy required to remove COD and produce H_2 of the SeaSET system.

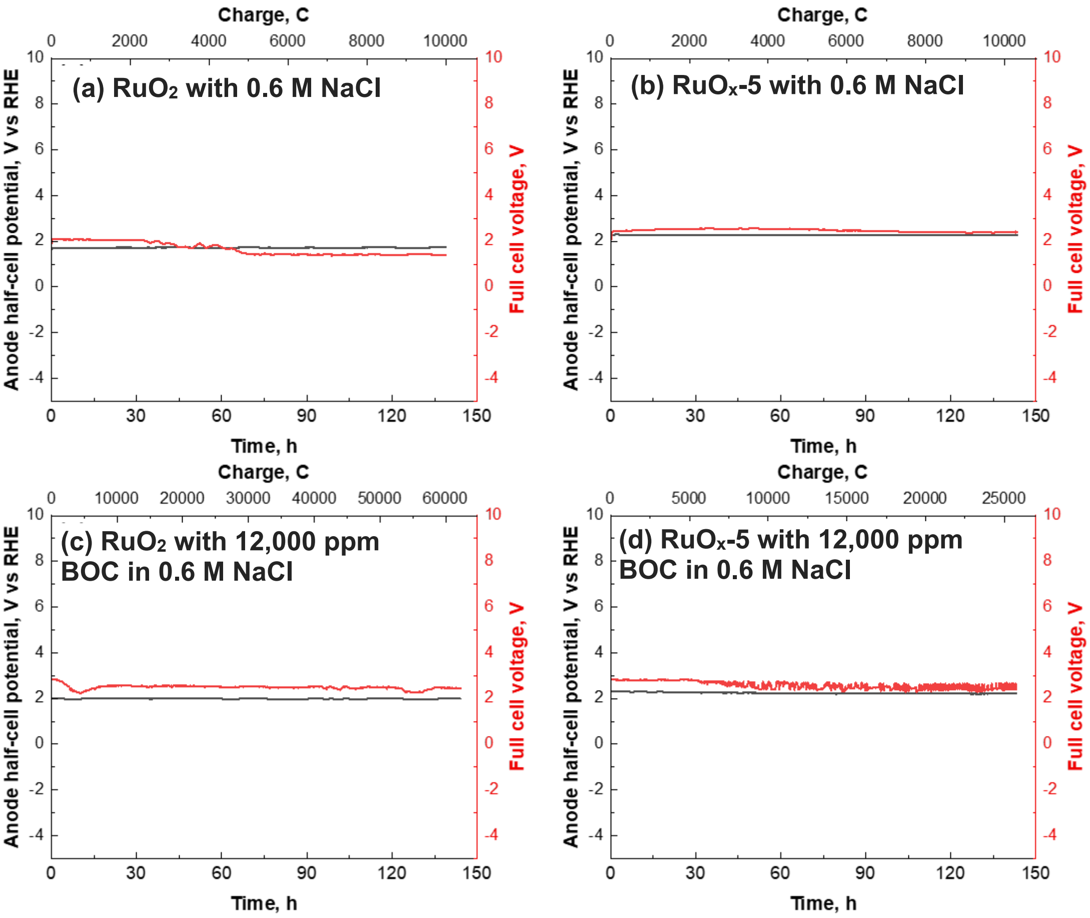


Figure 3. Stability of RuO_2 and RuOx-5 electrodes in (a and c) 0.6 M NaCl and (b and d) with 12,000 ppm of BOC at 2.2 V versus RHE.

Figure 3 depicts the half-cell potentials that remained stabled during the length of the experiment, suggesting that both RuO_2 and RuOx-5 did not degrade even in the presence of BOCs. The overall performance of RuO_2 and RuOx-5 anodes is compared in **Figure 4**, which shows that the cross-section area normalized current density of RuOx-5 is 6 and 2.5 times greater than that of the RuO_2 anode in 0.6 M NaCl without and with BOCs, respectively. The specific current (i.e., current normalized by the mass of Ru) of the RuOx-5 can reach up to 107.72 A/g_{Ru} in 0.6 M NaCl, which is nearly 12 times greater than the value obtained from the RuO_2 anode (8.99 A/g_{Ru}). These values are smaller in the presence of BOCs (44.88 A/g_{Ru} and 8.99 A/g_{Ru} for RuOx-5 and RuO_2, respectively), most likely due to the slower reaction rates for electrochemical oxidation of organic compounds compared to the OER rate (**Figure 1**). COD removal during the stability experiment after 100 h in the flow SeaSET electrolyzer is similar for both RuO_2 and RuOx-5 at 16.8% and 18.5%, respectively. However, the CE for COD removal is 2.5 times higher for RuO_2 than for RuO_x-5 (83.72% and 37.2%, respectively), suggesting that the increased reaction rate was most likely caused by an enhanced OER or CER reaction as opposed to the desirable oxidation of BOCs.

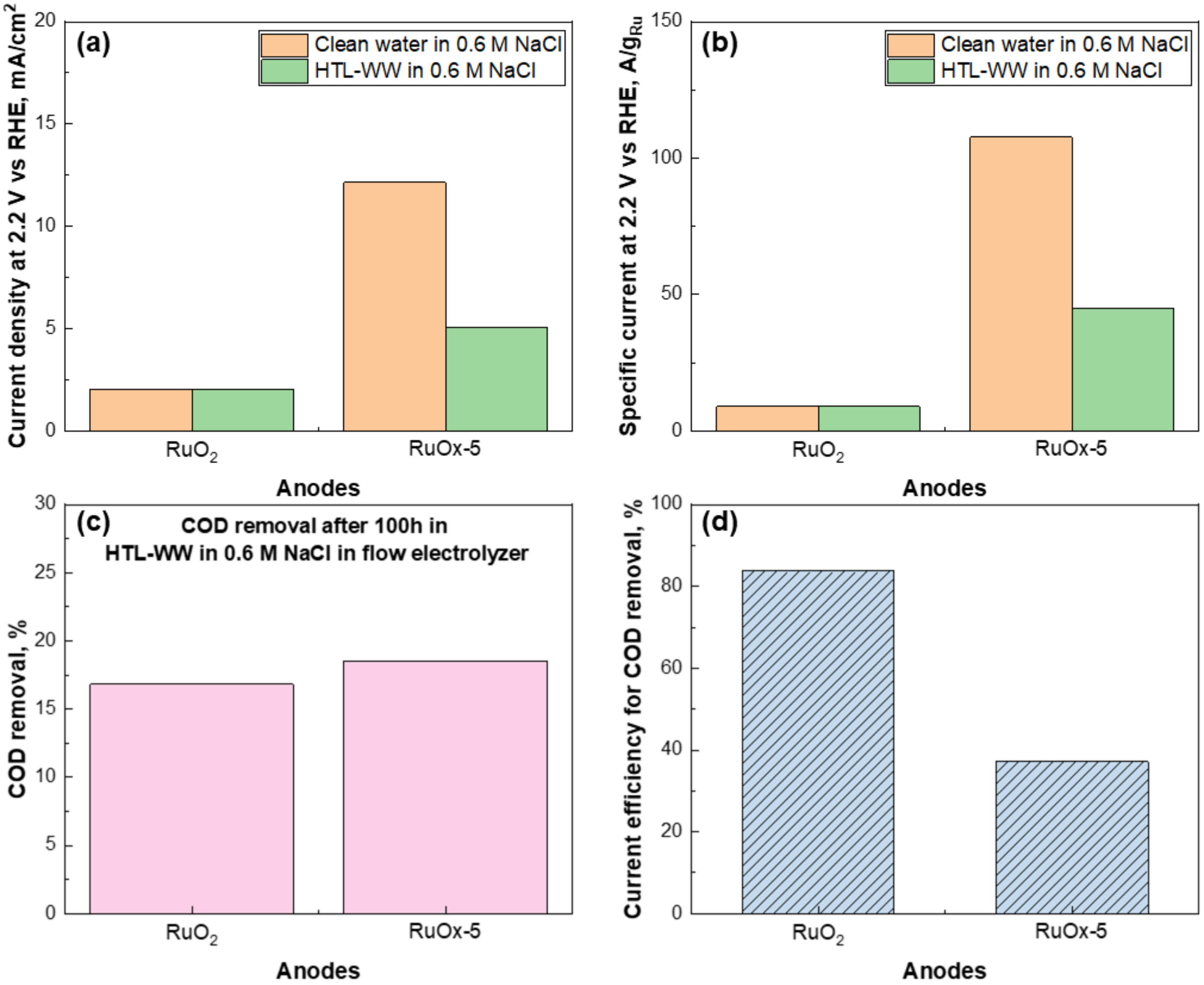


Figure 4. Comparison of the electrochemical performance of RuO_2 and RuOx-5 anodes in 0.6 M NaCl with and without 12,000 ppm of COD from BOCs with normalized (a) current density and (b) specific current at 2.2 V vs. RHE, (c) COD removal after 100 h of the stability test, and corresponding (d) CE for COD removal.

Table 1 summarizes the performance of the continuous-flow SeaSET electrolyzer with two different RuO_2 and RuOx-5 anodes and shows that the system can simultaneously produce H_2. However, the electrochemical performance (i.e., COD removal, CE, and kg of H_2 produced per kg of COD removed) differs for each anode evaluated. Here, within the same ≈100 h of experiments, the number of coulombs passed (i.e., charge) through the anode differs by a factor of 2.5 (> 25,750 C in RuOx-5 versus > 10,300 C in RuO_2). Thus, CE for COD removal is greater for RuO_2, which in turn leads to 2.5 times lower COD removal energy (10.0 and 25.0 kWh/kg COD for RuO_2 and RuOx-5, respectively. The H_2 generation energies for both anodes were similar (66.85 and 72.9 kWh/kg H_2).

Future work will focus on processing different Ru-based formulations at various potentials to identify correlations between the anode properties and electrochemical performance (i.e., COD removal, H2 production, and CE). Once we establish this correlation, we will test the most promising Ru-based formulations identified in the previous section to evaluate improvements in electrocatalytic performance.

Table 1. Performance of the RuO_2 and RuOx-5 anodes 0.6 M NaCl with and without 12,000 ppm of BOCs in a continuous-flow SeaSET electrolyzer at room temperature and atmospheric pressure.

Electrode	Charge Passed C	COD Removal, kWh/kg COD	[1]CE for COD Removal, %	H_2 Production, kWh/kg H_2	[2] Faradaic Efficiency[b] for H_2 Production %	Kilograms of H_2 Produced per Kilogram COD Removed
RuO_2	>10,300	10.0	83.7	66.6	79.6	0.15
RuOx-5	>25,750	25.0	37.2	72.9	112	0.34

[1] CE toward COD removal instead of other oxidation reactions.

[2] Faradaic efficiency toward H_2 production instead of other reduction reactions.

3.4 Electrode Stability

After performing the stability experiments, the RuO_2 anode was sectioned and mounted in epoxy for imaging. The cross-section through the coated area was imaged using SEM and EDX to evaluate how the morphology and composition of the anodes was changing after an electrochemical reaction. The cross-sectional analysis of the RuO_2 anode appears to show pitting corrosion potentially caused by penetration of the electrolyte through the RuO_2 layer where it corrodes the underlying TiO_2 (**Figure 5**). The RuO_2 layer appears to physically detach due to the pitting, causing erosion of the active material and a corresponding gradual deactivation of the surface. Future work will focus on performing the same analysis on the different Ru-based formulations to elucidate relationships between mechanical electrode degradation, electrochemical rection conditions, and anode formulation.

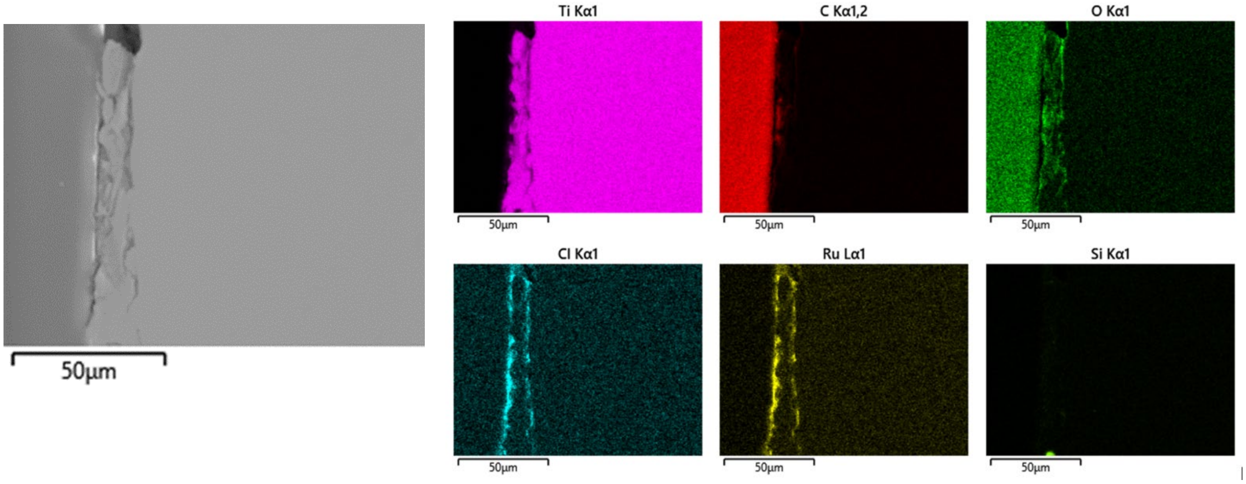


Figure 5. Scanning electron microscopy (SEM)/energy-dispersive X-ray spectroscopy (EDX) of a RuO_2 electrode cross-section after > 150 h in 0.6 M NaCl and > 150 h in 0.6 M NaCl with 12,000 ppm BOCs at 2.2 V vs. RHE.

4.0 Conclusions

In this study, we tested the electrochemical oxidation of model seawater containing BOCs in batch and continuous-flow electrolyzers. We successfully demonstrated that the CleanSET technology can be used to process BOC-containing seawater while simultaneously producing H_2 (SeaSET). The electrocatalytic performance depends on the Ru-based material formulation and electrocatalytic reaction conditions. Long-term experiments performed in the continuous-flow SeaSET electrolyzer showed that the electrocatalytic performance of both RuO_2 and RuOx-5 is stable for over > 200 h in 0.6 M NaCl with and without BOCs. While RuO_x-5 was more active than RuO_2, the CE for COD removal was greater for RuO_2, which in turn led to a 2.5 times lower COD removal energy (10.0 and 25.0 kWh/kg COD for RuO_2 and RuO_x-5, respectively). The H_2 generation energies for both anodes were similar (66.85 and 72.9 kWh/kg H_2). Preliminary SEM/EDX characterization shows that there was anode degradation due to corrosion pitting on the Ti support.

Future work will focus on understanding the correlation between electrocatalytic performance, reaction conditions, and Ru-based formulations. This correlation will be used to synthesize new, more efficient Ru-based formulations for the selective electrocatalytic oxidation of BOCs present in model 0.6 M NaCl solutions and real seawater.

5.0 References

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