

AESF Research Grant - G2429  
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**Summary:** Work this quarter was focused on optimizing the properties of the new catalyst for 6:2 FTS oxidation. By tuning the parameters of the catalyst synthesis step, higher removal of 6:2 FTS was achieved.

**Results:** Work focused on the deposition of a  $\text{Bi}_2\text{O}_3\text{-SnO}_2$  catalyst (BTO) on  $\text{Ti}_4\text{O}_7$  (i.e., BTO/ $\text{Ti}_4\text{O}_7$ ) using an electrodeposition method. The method utilized a pulse deposition method where a constant potential of -700 mV was held for a pulse time of between 10 to 50 ms, followed by a return to the open circuit potential for 1 s. This process was repeated for up to 3564 cycles. This method was chosen to minimize the size of the catalyst particles that were deposited on  $\text{Ti}_4\text{O}_7$ . The selection of -700 mV for the constant potential was based on linear sweep voltammetry data shown in **Figure 1**. Peaks in **Figure 1** show the potential at which Sn and Bi are deposited on the electrode surface.

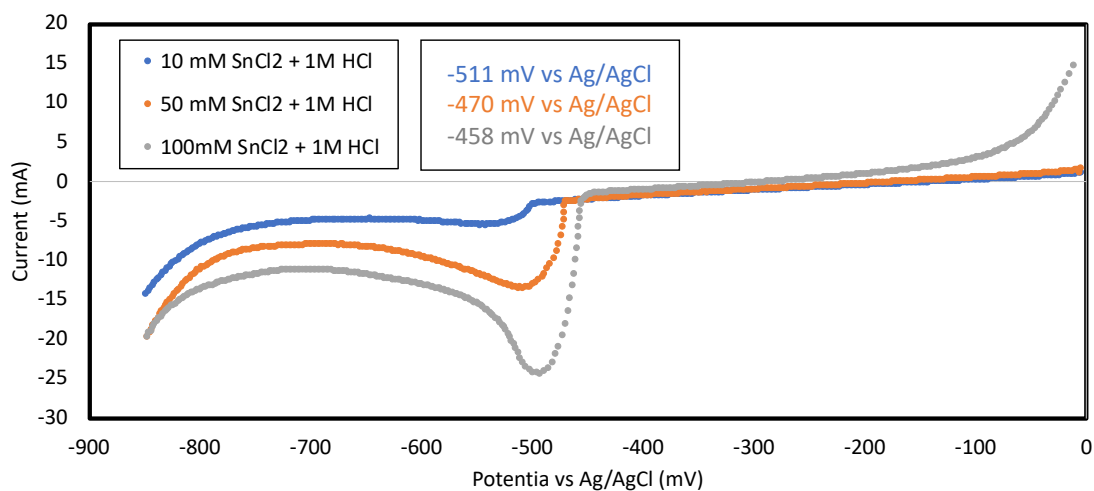
The first set of catalysts were prepared by changing the pulse time and the number of cycles. Pulse times of 10, 20, and 30 ms were tested with corresponding cycle number of 3564, 1782, and 188, respectively. Therefore, all three methods utilized a total deposition time of 35.6 s. The prepared samples were tested for 6:2 FTS removal in a flowthrough reactor with a hydraulic residence time was  $\sim 11$ s and as a function of potential (2.2. to 4.2 V/SHE). The reported removal was obtained in a single pass through the porous electrode. Results in **Table 1** show that 6:2 FTS removal and defluorination both increase with increasing pulse time. The highest removal (75.4%) and defluorination (19%) was achieved for the 30 ms pulse time at 4.2 V/SHE.

The next set of catalysts were prepared by varying the pulse time (20, 40, 50 ms), and the number of cycles was held constant at 3564. This provided total deposition times of 71, 143, and 178 s. Results in **Table 2** show once again that 6:2 FTS removal and defluorination both increase with increasing pulse time. The highest removal (>85%, below the detection limit) and defluorination (41%) was achieved for the 50 ms pulse time at 4.2 V/SHE. Interestingly, the performance at both 3.6 and 4.2 V/SHE were similar for 6:2 FTS removal, with a slightly higher defluorination at 4.2 V/SHE.

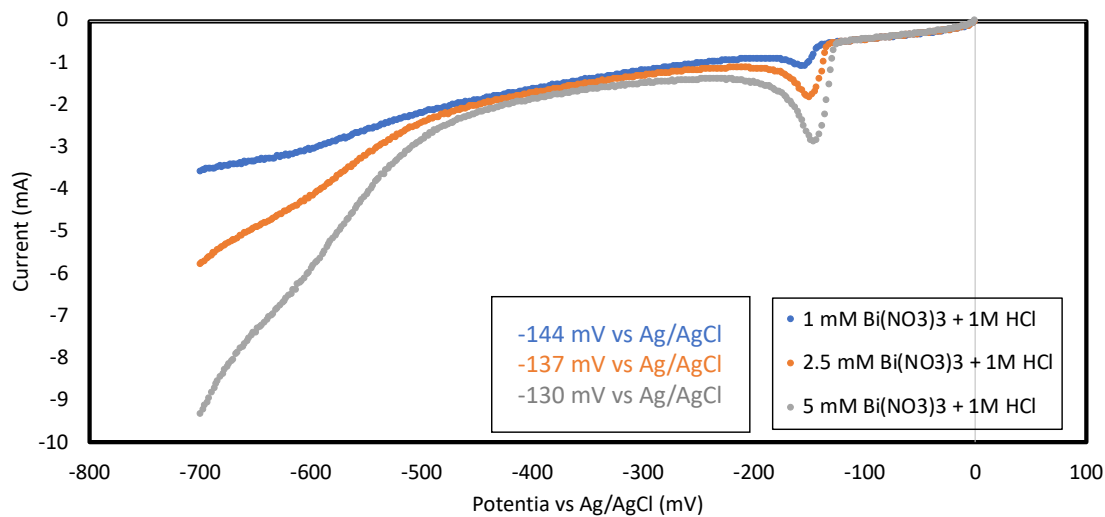
To assess the long-term performance of the BTO catalyst, a 5-hour experiment was conducted for the 40 ms pulse time and 3564 cycle number at 3.6 V/SHE. Results in **Table 3** show that both removal and defluorination decrease over time, which was attributed to catalyst leaching. Work is underway to determine methods to increase catalyst stability.

## Figures and Tables

a)



b)



**Figure 1:** Linear scan voltammetry for: (a) different concentration of SnCl<sub>2</sub>; (b) different concentration of Bi(NO<sub>3</sub>)<sub>3</sub>. Peaks correspond to the electrodeposition of the metals.

**Table 1.** 6:2 FTS removal and defluorination by BTO catalysts as a function of potential. Feed: 100  $\mu$ M 6:2 FTS + 100 mM NaClO<sub>4</sub>; flow rate = 240 LMH (11 s residence time)

Pulse time/cycle #	Potential (V/SHE)	Removal (%)	Defluorination (%)
10 ms/3564	2.2	6 $\pm$ 2	0
	2.9	5 $\pm$ 1	18 $\pm$ 8
	3.6	17 $\pm$ 2	10 $\pm$ 1
	4.2	57 $\pm$ 4	16 $\pm$ 1
20 ms/1782	2.2	9 $\pm$ 21	9 $\pm$ 6
	2.9	18 $\pm$ 3	10 $\pm$ 2
	3.6	55 $\pm$ 2	9 $\pm$ 1
	4.2	74 $\pm$ 1	12 $\pm$ 2
30 ms/1188	2.2	3 $\pm$ 6	25 $\pm$ 11
	2.9	16 $\pm$ 17	8 $\pm$ 1
	3.6	60 $\pm$ 3	14 $\pm$ 0.2
	4.2	75 $\pm$ 4	19 $\pm$ 1

**Table 2.** 6:2 FTS removal and defluorination by BTO catalysts as a function of potential. Feed: 100  $\mu$ M 6:2 FTS + 100 mM NaClO<sub>4</sub>; flow rate = 240 LMH (11 s residence time)

Pulse time/cycle #	Potential (V/SHE)	Removal (%)	Defluorination (%)
20 ms/3564	2.2	8.5 $\pm$ 8	0
	2.9	58 $\pm$ 14	3 $\pm$ 1
	3.6	80 $\pm$ 4	13 $\pm$ 2
	4.2	>85	18 $\pm$ 4
40 ms/3564	2.2	0	8 $\pm$ 7
	2.9	22 $\pm$ 16	7 $\pm$ 1
	3.6	76 $\pm$ 4	20 $\pm$ 3
	4.2	>85	32 $\pm$ 5
50 ms/3564	2.2	9 $\pm$ 8	4 $\pm$ 3
	2.9	49 $\pm$ 7	15 $\pm$ 6
	3.6	82 $\pm$ 1	30 $\pm$ 2
	4.2	>85	41 $\pm$ 2

**Table 3.** 6:2 FTS removal and defluorination by BTO catalysts as a function of time at 3.6 V/SHE. Feed: 100  $\mu$ M 6:2 FTS + 100 mM NaClO<sub>4</sub>; flow rate = 240 LMH (11 s residence time)

<b>Time</b>	<b>Removal (%)</b>	<b>Defluorination (%)</b>
30 min	78	18
45 min	64	16
1 hr	49	15
1.5 hr	39	16
2 hr	27	17
3 hr	21	16
4 hr	29	11
5 hr	29	10