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Supplementary Material to

Deposition efficiency in the preparation of ozone-producing nickel and antimony doped tin oxide anodes

Staffan Sandin¹, Alicia Cheritat¹, Joakim Backstrom², Ann Cornell¹

¹*Applied Electrochemistry, School of Chemical Science and Engineering, KTH Royal Institute of Technology, Stockholm, Sweden*

²*Department of Natural Sciences, Mid Sweden University, Sundsvall, Sweden*

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1 Chemicals and instruments

Table 1: Chemicals and materials

Name	Chemical formula	Maker
Hydrochloric acid 37 %	HCl	Merck
Titanium discs, grade 2	Ti	-
Tin tetrachloride pentahydrate, pro analysi	$\text{SnCl}_4 \cdot 5 \text{H}_2\text{O}$	Sigma Aldrich
Tin dichloride dihydrate, pro analysi	$\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}$	Merck
Antimony trichloride, ACS reagent $\geq 99\%$	SbCl_3	Sigma Aldrich
Nickel dichloride hexahydrate, pro analysi	$\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$	Merck
Ethanol, analytical grade 99.5 %	$\text{C}_2\text{H}_5\text{OH}$	Solveco
n-propanol, ACS reagent $\geq 99.5\%$	$\text{C}_3\text{H}_8\text{O}$	Sigma Aldrich
n-butanol, ACS reagent $\geq 99.4\%$	$\text{C}_4\text{H}_{10}\text{O}$	Sigma Aldrich
Sulfuric acid, 98 %	H_2SO_4	Sigma Aldrich
Hydrogen fluoride 50 %	HF	-

Table 2: Instruments

Component	Maker	Model
Reference electrode, Ag/AgCl sat.	Radiometer	XR400
Potentiostat	PAR	273A
SEM	Hitachi	S-4800
XRF	Philips	PW2400
XRD	Bruker	D2 Phaser
TG-DSC	Netzsch	STA 449 F3
UV-vis spectrophotometer	Expedeon	Versastat

2 TG-DSC analysis

The oxide formation process (*i.e.* heating of salts and solution) was characterized using coupled TG-DSC (Thermogravimetry-Differential Scanning Calorimetry). The TG-DSC instrument was calibrated both for temperature and heat flow prior to use by heating pure metals of Zn, Al, Sn, and In at the same heating rate (5 K/min) and in the same temperature range 25-600 °C as the experiments were performed. The calibration was made in both nitrogen and air atmosphere to make sure that none of the calibration standards were oxidized during calibration in air. All TG-DSC runs were made in dry air at atmospheric pressure. Figures 1 and 2 shows data from repeated trials of tin salts with and without Sb and Ni doping dissolved in ethanol and n-propanol. Figure 3 shows TG data from heating of the nickel salt and the salt dissolved in ethanol and n-propanol.

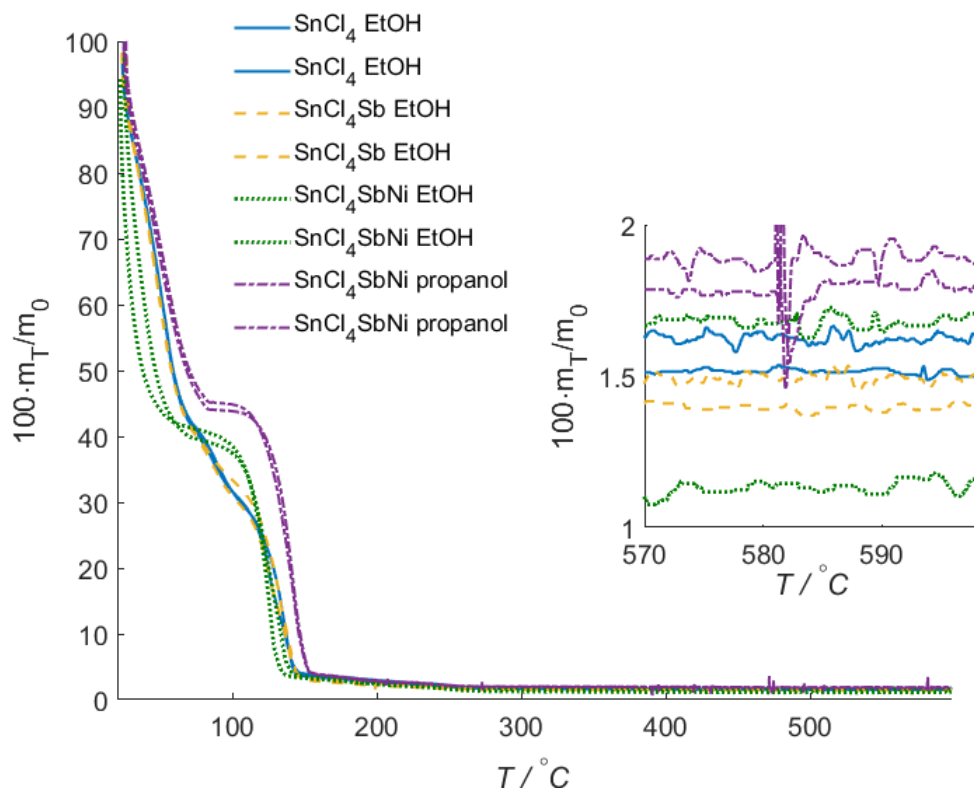


Figure 1: $\text{SnCl}_4 \cdot 5 \text{H}_2\text{O}$ with and without Sb and Ni doping in solutions of EtOH and n-propanol. Repeated trials

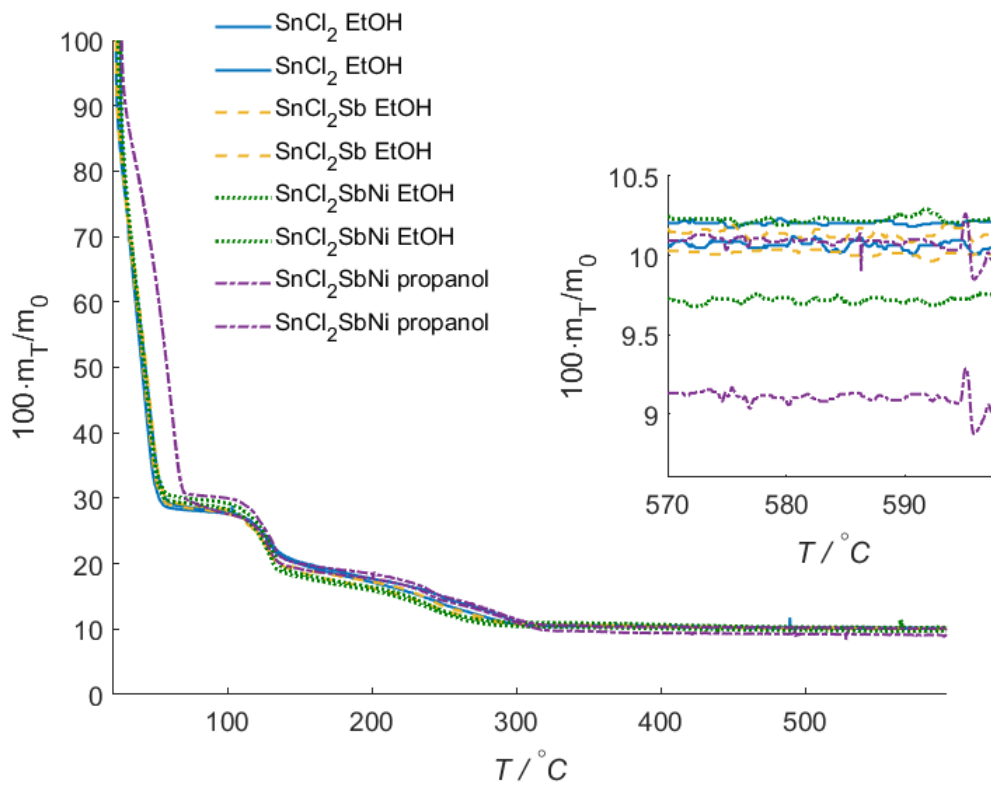


Figure 2: $\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}$ with and without Sb and Ni doping in solutions of EtOH and n-propanol. Repeated trials

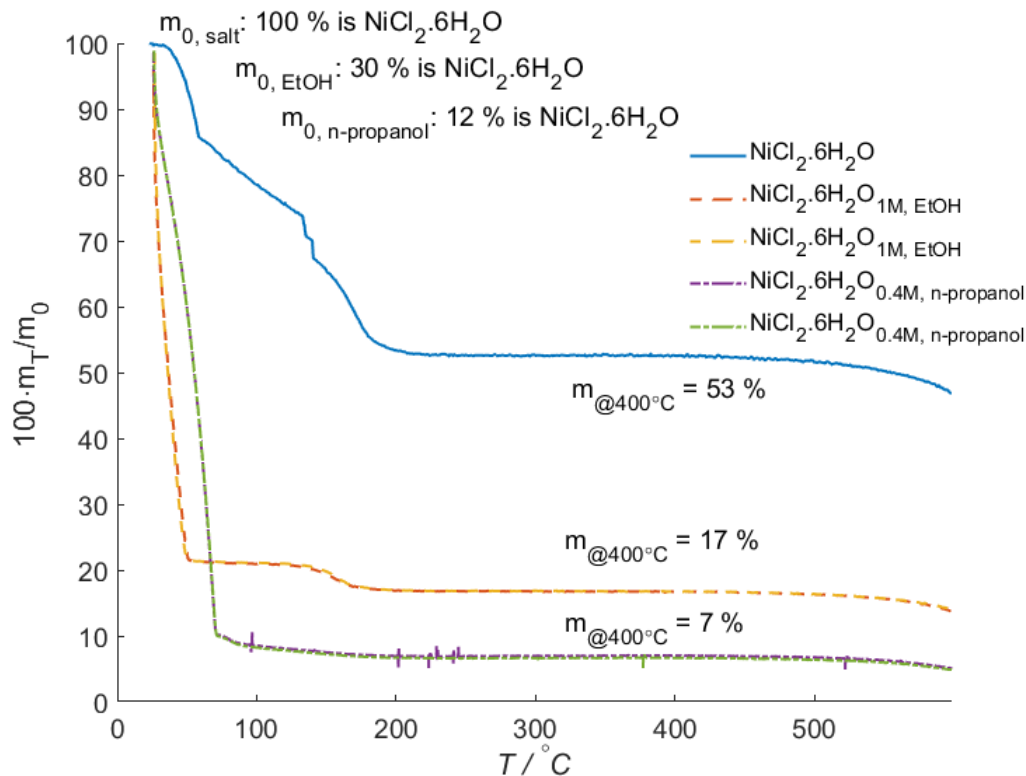


Figure 3: TG data from heating of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ as salt and dissolved in EtOH and n-propanol

3 Electrode preparation

Two batch of electrodes were made. The first batch with the intention of comparing the $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ based electrodes with the same composition for both (1000:16:2 in molar ratios of Sn:Sb:Ni). The second bath was made with the intention of making electrode coatings based on the divalent salts with a variation of the dopant concentration to see the influence on the formation of ozone. When making the first batch it was seen that the tetrachloride based electrode had a very low increase in loading per layer coated by spin coating. In the second batch the tetrachloride based electrodes were therefore prepared by dripcoating. Below follows the preparation procedures for the two batches.

3.1 Batch 1

Stem solutions of concentrations 2, 0.1 and 0.1 M was prepared for the tin, antimony and nickel salts, respectively. All salts were dissolved in ethanol and no HCl was added as no precipitation was seen after stirring for about 3 hours. These stem solutions were then mixed to the molar ratio 1000:16:2 with a Sn concentration of 1 M. Upon mixing the antimony solution with the $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ solution a white, gel-like, precipitate was formed. The precursor solution was stirrer for approximately 3 hours after which the precipitate was gone.

Titanium substrates 0.5 mm in thickness and 59 mm in diameter were prepared as follows:

- Cleaned with detergent and rinsed with MilliQ water

- Pickled in a room temperature bath of hydrogen fluoride (diluted to 1 %) for 2 minutes
- Rinsed thoroughly in MilliQ water
- Ultrasonic bath with detergent for approximately 10 minutes
- Rinsed thoroughly in EtOH and MilliQ water
- Dried at 80 °C for 40 - 60 minutes

The clean titanium substrates were coated with the precursor solutions by spin-coating at 500 rpm for 20 seconds followed by 1500 rpm for 30 seconds. After application of precursor solution, the electrodes were first dried at 80 °C for 10 minutes and then calcinated at 500 °C for 10 minutes. The coating was repeated 5 times. After the final layer, the electrodes were calcined at 500 °C for 60 minutes. Three electrode samples was prepared using each type of precursor solution. The loading increase per layer can be seen in Figure 8 in the manuscript.

3.2 Batch 2

Stem solutions of concentrations 2, 0.4 and 0.05 M was prepared for the tin, antimony and nickel salts, respectively. Propanol was used as solvent for $\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}$, SbCl_3 , $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$, while $\text{SnCl}_4 \cdot 5 \text{H}_2\text{O}$ was dissolved in ethanol. The stem solutions were then used to mix precursor solutions of molar ratios 1000:16:2, 1000:32:4, 1000:64:8, and 1000:108:16 for the solutions using $\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}$ and only 1000:16:2 for the solution using $\text{SnCl}_4 \cdot 5 \text{H}_2\text{O}$. All solutions had a Sn concentration of 1 M. Upon mixing the $\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}$ based precursor solutions, a precipitate was formed. As this did not dissolve by mixing, 37 % HCl was added until the solutions cleared (3 mL to a total volume of 50 mL). The titanium substrates (0.5 mm in thickness and 59 mm in diameter) were prepared in the same way as described for Batch 1. The clean titanium substrates were coated by spin-coating with the precursor solutions using $\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}$ and by drip coating for the $\text{SnCl}_4 \cdot 5 \text{H}_2\text{O}$ solution. The spin coating was made at 500 rpm for 20 seconds followed by 1500 rpm for 30 seconds and the drip coating was made by dripping solution on the substrates followed by manually tilting them to spread the solution as equally as possible. After application of precursor solution, the electrodes were first dried at 80 °C for 10 minutes and then calcinated at 500 °C for 10 minutes. The coating was repeated 7 times. After the final layer, the electrodes were calcined at 500 °C for 60 minutes. Two electrode samples was prepared using each type of precursor solution. The loading increase per layer can be seen in Figure 4.

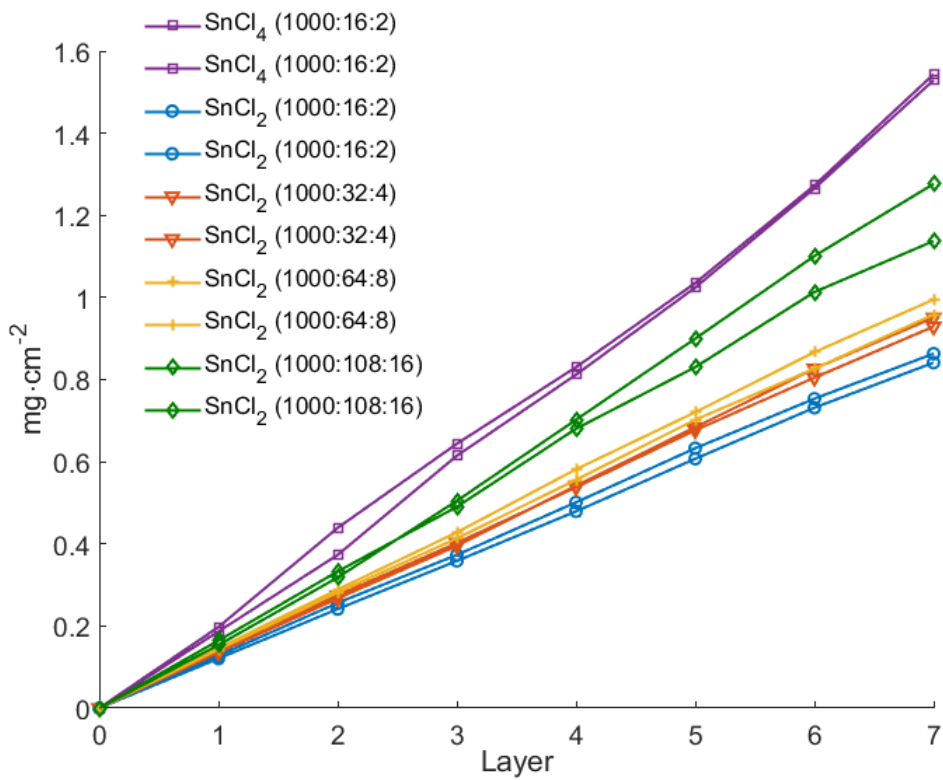


Figure 4: Increase in loading for batch 2 electrodes