

ELECTRODEPOSITION OF $\text{Co}_{(1-x)}\text{Sb}_3$ IN CITRATE SOLUTIONS: EFFECT OF DOPING WITH Co AND Te

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INTRODUCTION

CoSb_3 is a compound with a skutterudite structure which has been identified as a potential new material for thermoelectric materials at intermediate temperatures (400-700 °C). The efficiency of a thermoelectric material is determined by its dimensionless thermoelectric figure of merit ZT that can be expressed below.

$$Z \cdot T = \frac{S^2 \cdot \sigma \cdot T}{\kappa}$$

S is Seebeck coefficient
 σ is electrical conductivity
 κ is thermal conductivity
 T is temperature

GOOD THERMOELECTRIC MATERIAL

Doping effect

Optimize the electrical conductivity and effectively scatter phonons

Ni Co
Te Sb

RESULTS AND DISCUSSION

Cyclic voltammetry

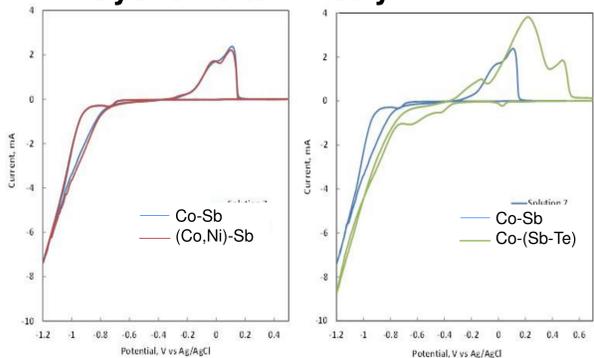


Figure 5: Cyclic voltammetry of Au in Co-Sb solution and Ni and Te-ion solution at 5 mV/s

CV of Au in Co-Sb and (Co-Ni)-Sb show two oxidation peaks and no clear reduction peaks. Hydrogen evolution is significant for this system and may overlap the deposition peak. Adding Ni ions in the electrolyte does not visibly affect the CV. Ni and Co form solid solutions over the entire concentration range and this may be the reason why the two CVs are similar.

Addition of Te ions drastically changes the CV, i.e. additional deposition and stripping peaks appear.

The potential range for CV in Te-containing Co-Sb solution was extended in the positive direction from 0.5 to 0.7 V vs. Ag/AgCl to allow for the deposit to be removed from the surface during stripping.

Deposition-stripping experiments

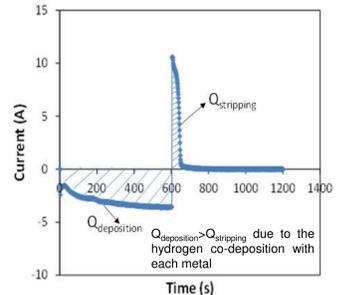


Figure 6: Current evolution during a deposition-stripping experiment at a fixed potential

Faraday's Law

$$m = \frac{Q \cdot M}{F \cdot z}$$

$$Q = i \cdot t$$

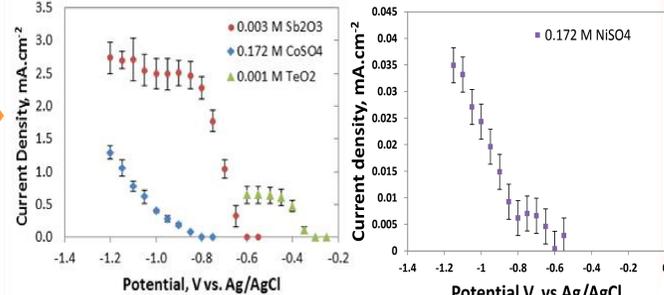


Figure 7: Deposition rates of Co, Sb, Te and Ni in citrate solutions

Morphology and composition of doped Co-Sb films and nanowires

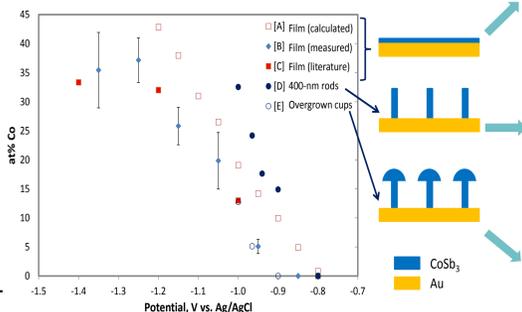


Figure 9: Composition of Co deposited from citrate solution with 0.172 M Co (II) and 0.006 M Sb (III): a) film prediction based on single solutions of Co (II) and Sb (III), b) film experimental results in solution with both Co (II) and Sb (III), c) film adjusted results from bibliography, d) 400 nm rods and e) overgrown mushroom caps.

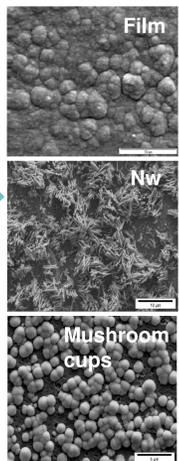


Figure 10: SEM images of Co-Sb in different configurations

Table 1: EDS results obtained for Ni and Te doped nanowires

Shown are relatively uniform deposits on the entire membrane surface, including holes. Local variations in morphology may be associated with the particular nature of the nanostructured Au surface and by H_2 evolution

Steps for nanowires formation:

1. Nucleation and growth of the nuclei inside pores
2. Continuous growth of nucleation which overlap inside the template
3. Nanowires continuous growth into mushroom cups.

Composition, at. %	Co-Sb	(Co-Ni)-Sb	Co-(Sb-Te)
Sb L	1.94+/-0.05	1.55+/-0.37	3.615+/-0.27
Co K	1.87+/-0.16	1.61+/-0.43	3.34+/-0.05
Ni K	-	0.13+/-0.09	-
Te K	-	-	0.39+/-0.05
(Co,Ni)/(Sb,Te)	0.96+/-0.06	1.12+/-0.06	0.83+/-0.05

EXPERIMENTAL

Set-up working electrode

Gold sputtered polycarbonate track-etched (PCTE) membranes were used as substrates for deposition. The membranes are 10 μm thick with 400 nm pores.

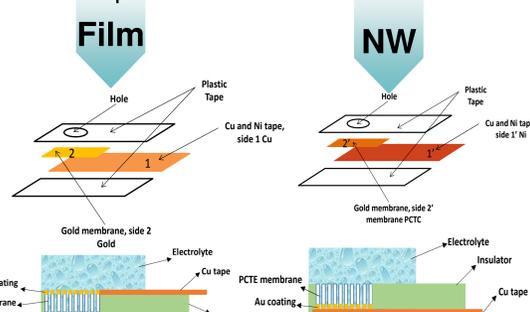


Figure 1: Schematic 3D (up) and cross section (down) set up of the working electrode for film and nanowire configuration.

Experimental design

- 1 Electrolyte
- 2 Work electrode
- 3 Reference electrode Ag/AgCl
- 4 Counter electrode, gold wire
- 5 Potentiostat Pine Instrument
- 6 Heater and Magnetic agitator

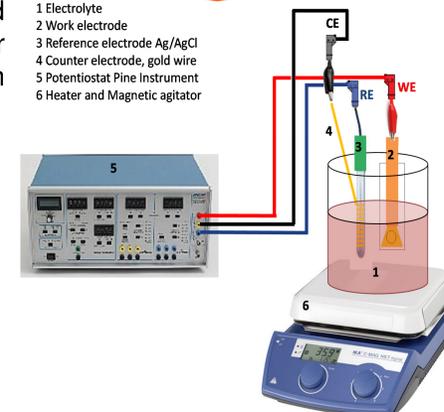


Figure 2: Experimental set-up

Pretreatment

Electrochemical treatments were performed in 50 mM H_2SO_4 in order to clean the Au surface and to ensure identical surface conditions before each experiment.

Figure 3: Au surface treatment steps

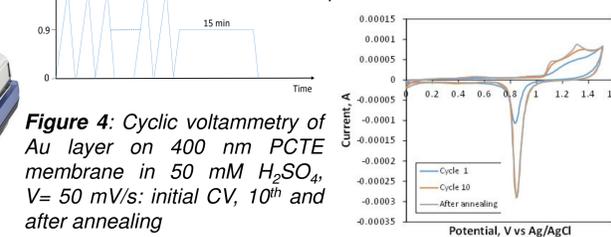


Figure 4: Cyclic voltammograms of Au layer on 400 nm PCTE membrane in 50 mM H_2SO_4 , $V = 50 \text{ mV/s}$: initial CV, 10th and after annealing

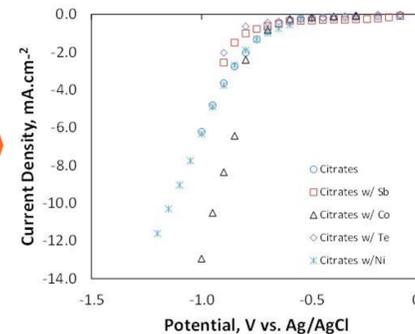


Figure 8: Hydrogen evolution in different citrate solutions

Deposition of Co is controlled by the electrochemical reaction at the cathode, while Sb and Te are controlled by diffusion. Deposition of Ni occurs at smaller current densities than other elements and is also controlled by surface reaction.

The influence of H_2 evolution on the co-deposition process is an important issue due to the proximity of their reaction potentials and possible interferences.

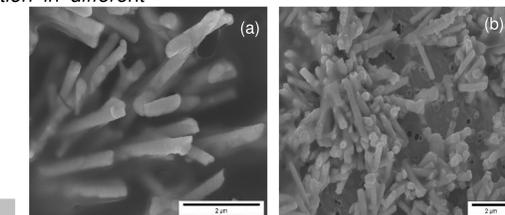


Figure 11: SEM image of Te-doped (a) and Ni-doped (b) Co-Sb nanowires

CONCLUSIONS

- Addition of Ni in the electrolyte doesn't affect the CV, Co-Ni forms an alloy, however, addition of Te affects the CV which shows 2 different peaks.
- Ni and Co deposition are controlled by reaction but Sb and Te are controlled by mass transfer.
- H_2 evolution is more important for Co and Ni deposition due to their potential being close to the H_2 evolution potential.
- Amount of Co is higher in nanowires than in films, or mushroom cups, due to the slow Sb deposition rate as limited by diffusion
- Ni and Te electrochemical doping of Co-Sb system affects the composition of the deposit but it has no effect on the nanowire morphology