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The electrodeposition of Zn-Mo and Zn-Sn-Mo alloys from citrate electrolytes

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The electrodeposition of Zn-Mo and Zn-Sn-Mo alloys from citrate electrolytes

Plan of presentation

1. Brief introduction
   - → Why Zn-Mo and Zn-Sn-Mo alloys ?
   - → How to do it ?
2. What exactly I made during last two years?
   - → First year
   - → Second year
   - → Conclusion
3. Further plans

Why Zn-Mo and Zn-Sn-Mo alloys ?

Zn-Mo and Zn-Sn-Mo alloys are proposed as environment friendly corrosion protective coatings.

Especially interesting as replacement materials for:

- cadmium layers

- zinc coatings with Cr(VI) based conversion layer

How to do it?

The main problems to solve are the following:

1. developing the stable baths for electrodeposition of **Zn-Mo** and Zn-Sn-Mo alloys
2. determining the kinetics and mechanism of electroreduction of citrate complexes
3. modelling the electrodeposition process
4. determining the optimal ranges of the electrodeposition parameters
5. optimizing the corrosion resistance of the **Zn-Mo** and Zn-Sn-Mo layers

What exactly I made during last two years?

First year of Ph.D. studies

1. I developed the stable baths for electrodeposition of Zn-Sn and Zn-Sn-Mo alloys
   - → on the basis experimental verification of thermodynamic models of citrate systems
     - → Cyclic voltammetry
     - → Rotating disc electrode
     - → Spectrophotometry UV-Vis
2. I determined the optimal ranges of the electrodeposition parameters enabling to obtain Zn-Sn and Zn-Sn-Mo alloy layers
   - → Potentiostatic and galavanostatic deposition at different parameters
     - → Electrolyte composition
     - → pH
     - → Rotating disc electrode speed
     - → Charge
     - → Substrate (Cu, Fe)
   - → Investigation of obtained coatings
     - → Scanning electrone microscopy (SEM)
     - → Energy Dispersive X-ray Spectrosmetry (EDS)
     - → Wavelength dispersive x-ray fluorescence spectrometry (WDXRF)
     - → Glow discharge optical emission spectrometry (GDOES)
3. I determined the kinetics and mechanism of electroreduction of citrate complexes (in Zn-Sn , Zn-Sn-Mo systems)
   - → Linear voltammetry
   - → Cyclic voltammetry
   - → Rotating disc electrode

What exactly I made during last two years?

Second year of Ph.D. studies

1. I developed the stable baths for electrodeposition of Zn-Mo alloys
   - → Cyclic voltammetry
   - → Rotating disc electrode
   - → Spectrophotometry UV-Vis

2. I determined the optimal ranges of the electrodeposition parameters enabling to obtain Zn-Mo alloy layers
   - → Potentiostatic and galavanostatic deposition at different parameters
     - → Electrolyte composition
     - → pH
     - → Rotating disc electrode speed
     - → Charge
     - → Substrate (Cu, Fe)
   - → Investigation of obtained coatings
     - → Scanning electrone microscopy (SEM)
     - → Energy Dispersive X-ray Spectrosmetry (EDS)
     - → Wavelength dispersive x-ray fluorescence spectrometry (WDXRF)
     - → Glow discharge optical emission spectrometry (GDOES)
     - → **X-ray Photoelectron Spectroscopy (XPS)**

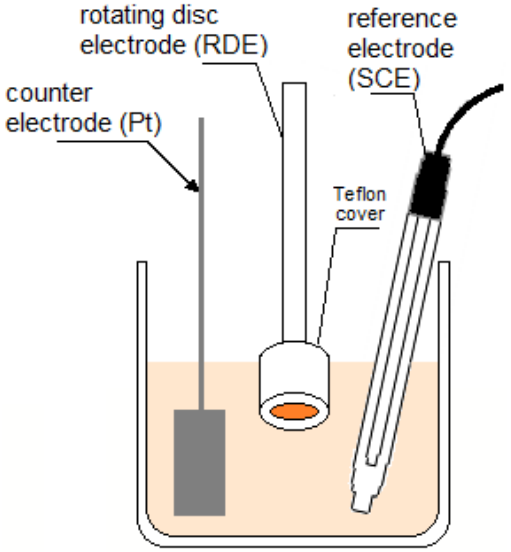
3. I determined the kinetics and mechanism of electroreduction of citrate complexes (in Zn-Mo systems)
   - → Linear voltammetry
   - → Cyclic voltammetry
   - → Rotating disc electrode

Experimental

1) Analysis of the mechanism of electrochemical co-deposition of molybdenum with zinc from citrate solutions .

2) Experimental determination of parameters of the electrochemical deposition of Zn-Mo alloy layers from citrate solutions.

3) Characterization of surface of obtained coatings.



working electrode

Cu Fe

<u>Variable parameters:</u>

potential: -1,2 ÷ -2,3 V vs. SCE

concentration of $C_6H_5Na_3O_7 \cdot 2H_2O$ [(1)] : 0,25 ÷ 0,65 mol/dm^3

[(1)] Denoted in text as Na_3Hcit (where cit= $C_6H_4O_7$),

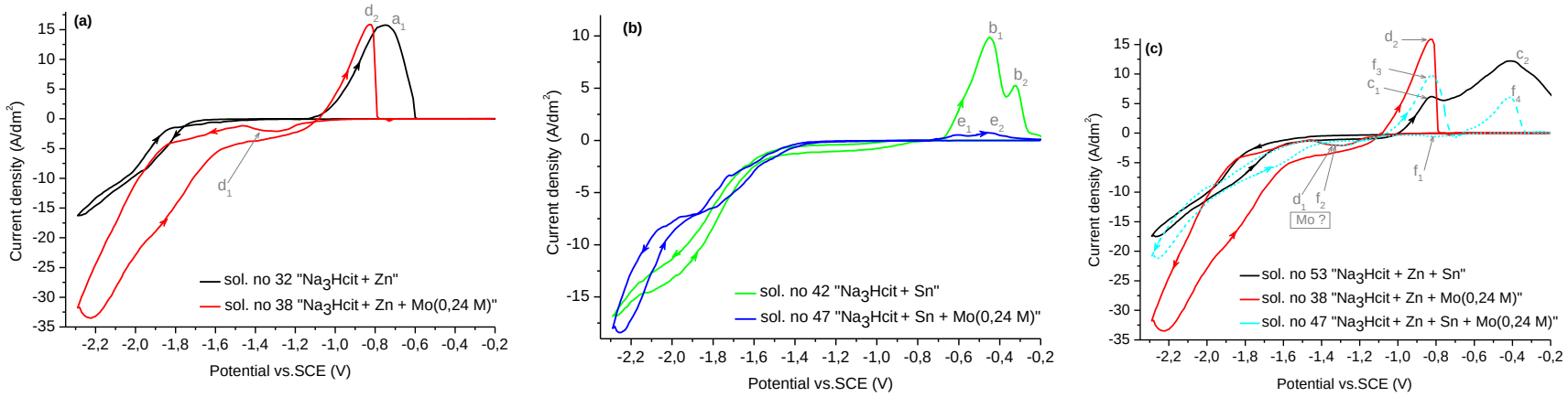
Na_2MoO_4: 0,02 ÷ 0,30 mol/dm^3

$ZnSO_4 \cdot 7H_2O$: 0,08- 0,20 mol/dm^3

pH: 1 ÷ 9

RDE speed: 16 ÷ 68 rad/s

Results



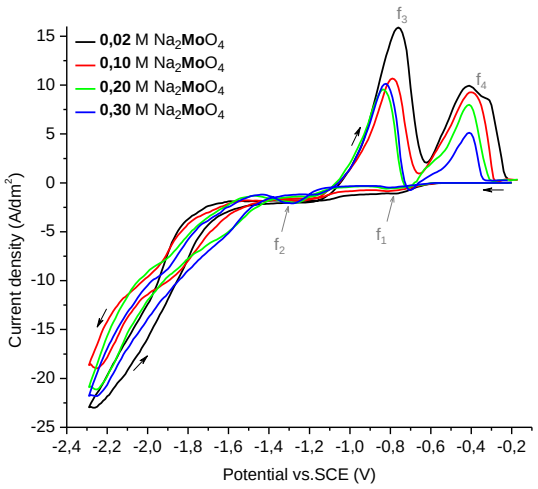
Cyclic voltammograms measured on a Cu substrate in solutions of various composition, at scan rate =20 mV/s, ω= 40 rad/s, pH=5.
Arrows indicate scan direction.

Table 2. The assignment of voltammetric peaks to processes

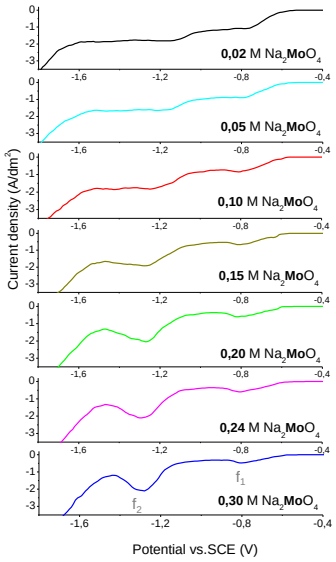
Reduction of molybdenum	Oxidation of zinc	Oxidation of tin
d_1	a_1	b_1 (to Sn II) , b_2 (to Sn IV)
f_1, f_2	c_1	c_2
g_1,g_2	d_{-2}	e_1(to Sn II), e_2(to Sn IV)
	f_3	f_4

H. Kazimierczak, P. Ozga, Electrodeposition of Sn–Zn and Sn–Zn–Mo layers from citrate solutions, Surf. Sci. (2012), http://dx.doi.org/10.1016/j.susc.2012.08.010

Results

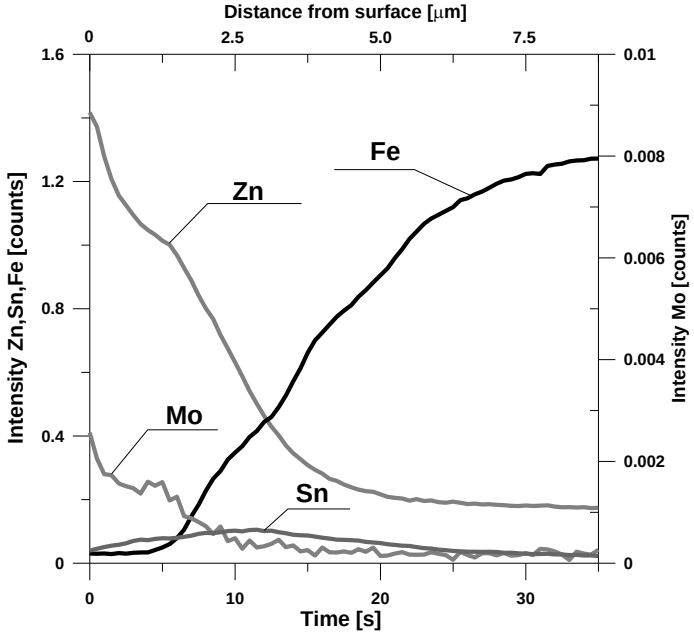


Selected part of cathodic voltammetric curves:



Cyclic voltammograms measured on a Cu substrate in solutions containing:0.65 M Na_3HCit + 0.08 M $SnSO_4$ + 0.16 M $ZnSO_4$ + 0.16 M Na_2SO_3 and various concentrations of Na_2MoO_4 which are given on the graph. Scan rate = 20 mV/s, ω = 40 rad/s, pH = 5.

Chemical profile analysis of Zn-Sn-Mo layer obtained from solution no. 62 on steel substrate (0.24 M Na_2MoO_4 ω=16 rad/s, t=20°C, j=6 A/dm², 100C).



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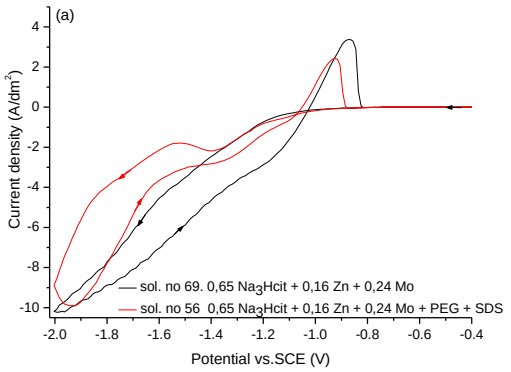
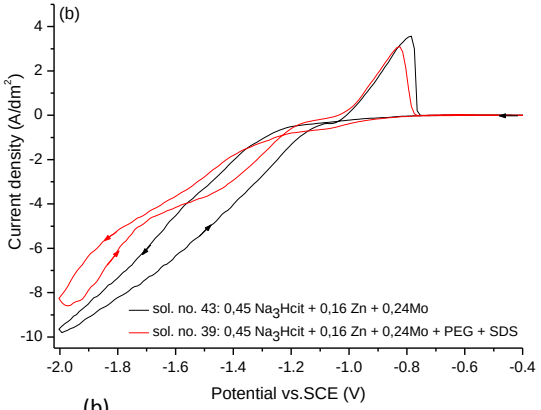
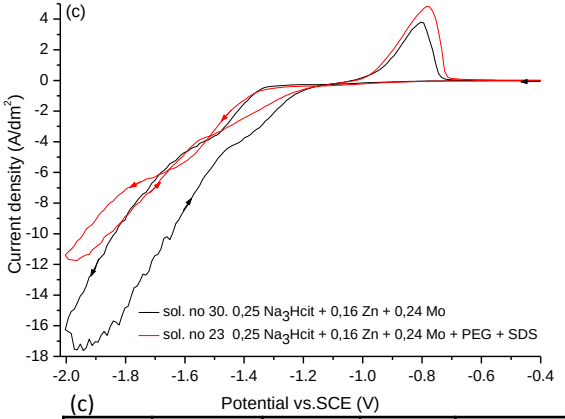
Results







(a)

solution no.		cit [mol/dm3]		Potential vs.SCE	contents of Mo in layers [wt. %]	current efficiency [%]
69.	without PEG and SDS	0.65	Cu substrate	-1.30	0.00	2.36
				-1.40	0.00	2.18
				-1.60	0.00	13.40
				-1.80	0.00	16.35
				-2.00	0.00	11.63
56.	with PEG and SDS	0.65	Cu substrate	-1.30	0.00	3.66
				-1.40	3.36	11.05
				-1.60	0.00	4.43
				-1.80	0.00	6.79
				-2.00	0.00	9.03
			Fe substrate	-1.30	0.00	2.42
				-1.40	2.25	8.39
				-1.60	0.00	3.36
				-1.80	0.00	7.08
				-2.00	0.00	7.20

(b)

solution no.		cit [mol/dm3]		Potential vs. SCE	contents of Mo in layers [wt. %]	current efficiency [%]
43.	without PEG and SDS	0.45	Cu substrate	-1.30	6.79	12.22
				-1.40	5.02	17.84
				-1.60	1.93	12.06
				-1.80	0.00	17.47
				-2.00	0.00	16.64
39.	with PEG and SDS	0.45	Cu substrate	-1.30	5.01	20.49
				-1.40	5.53	13.00
				-1.60	2.96	14.13
				-1.80	0.00	5.25
				-2.00	0.00	14.10
			Fe substrate	-1.30	3.13	18.56
				-1.40	5.75	11.87
				-1.60	1.37	8.72
				-1.80	0.00	7.79
				-2.00	1.31	9.49

(c)

solution no.		cit [mol/dm3]		Potential vs. SCE	contents of Mo in layers [wt. %]	current efficiency [%]
30.	without PEG and SDS	0.25	Cu substrate	-1.30	9.00	49.40
				-1.40	12.17	47.54
				-1.60	5.27	21.47
				-1.80	1.09	19.19
				-2.00	0.88	18.11
23.	with PEG and SDS	0.25	Cu substrate	-1.30	7.71	64.51
				-1.40	9.00	40.37
				-1.60	6.47	24.71
				-1.80	3.27	14.69
				-2.00	2.10	11.36
			Fe substrate	-1.30	7.65	67.41
				-1.40	11.75	34.21
				-1.60	5.93	25.50
				-1.80	0.00	7.32
				-2.00	0.00	12.81

Effect of sodium citrate concentration and surface active additives on electrodeposition on molybdenum.

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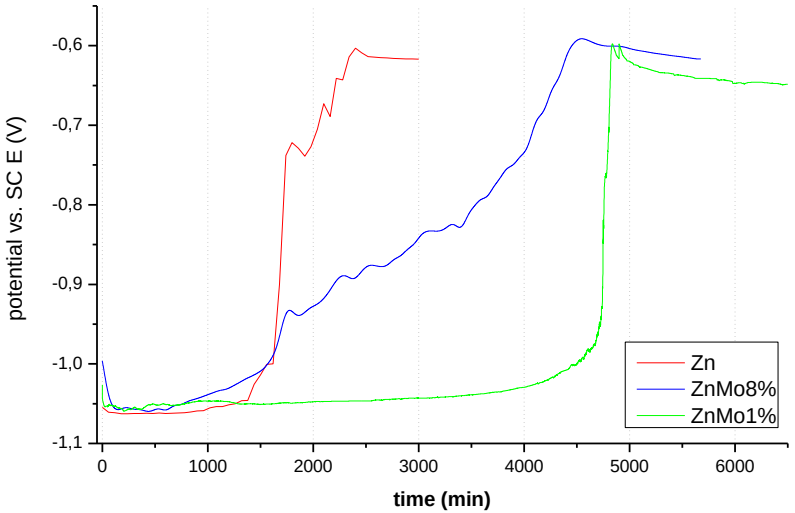
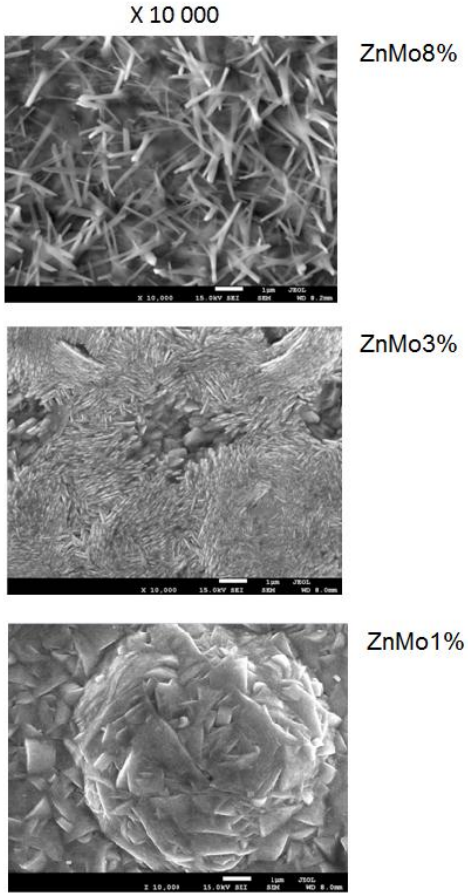
Results



OCP curves of Zn and Zn-Mo coatings during immersion in 5% NaCl solution at room temperature



SEM images of Zn-Mo coatings(with different contents of Mo) deposited from citrate baths with various concentrations of $MoONa_2MoO_4$, pH=5, ω=16rad/s, E=-1.3 V (ZnMo8%, ZnMo3%), E=-1.5 V (ZnMo1%)

Conclusions

- It is possible to electrodeposit alloy layers based on zinc and tin with additives of molybdenum from citrate electrolytes.
- It is possible to electrodeposit Zn-Mo alloy layers from the aqueous citrate solutions.
- Optimal conditions for electrodeposition from the citrate baths studied are in the slightly acid range (pH about 5).
- The results of chemical profile analysis (WDXRF) prove the presence of molybdenum in deposits. The highest contents of Mo in the investigated layers was 14.45 wt.%.
- The results of voltammetric studies and chemical profile analysis indicate some connections in the electrodeposition of Zn and Mo which is not observed in the case of electrodeposition of Sn and Mo, but further studies need to be conducted for better understanding of the mechanism and kinetics of electrodeposition of Sn-Zn-Mo alloy layers.
- The content of molybdenum in Zn-Mo layers and the current efficiency of electrodeposition increases with the decrease of sodium citrate concentration in the electrolyte.
- The addition of molybdenum improve the corrosion resistance of zinc layers

Further plans

Focus on Zn-Mo citrate system

1. Understadning and describing the kinetics and mechanism of electroreduction of zinc and molybdenum citrate complexes
2. Determining the optimal ranges of the electrodeposition parameters
3. Characterization of obtained Zn-Mo layers
   - → study of the morphology (SEM)
   - → study the surface composition (WDXRF)
   - → XRD phase analysis
   - → study of the element distribution in cross-section of layers (study of the layers growing) (EDS, GDOES)
   - → study of the electronic states of compounds in the alloy by XPS.
   - → and if molybdenum is fully reduced- High Resolution Transmission Electron Microscopy may be used for determination of Mo form (if it is intermetallic compound, solid solution of certain phase, etc.)
4. Study the corrosion and optimizing the corrosion resistance of the Zn-Mo layers
   - → Salt spray test
   - → Open cicuit potential (OCP)
   - → Linear polarization (LP)
   - → Electrochemical Impedance Spectroscopy (EIS)
   - → Phase changes during the process of corrosion (XRD)