

Metal and alloy composites with carbon nanomaterials obtained by electrodeposition from deep eutectic solvents

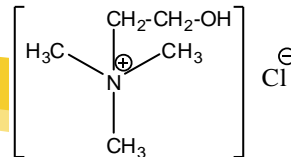
Liana Anicai^a, Aurora Petica^a, Stefania Costovici^b, Oana Brincoveanu^a, Aida Ghiulnare Pantazi^a, Danut Balan^a, Marius Enachescu^a, Teodor Visan^{a,c}

^a*Center of Surface Science and Nanotechnology, University Politehnica of Bucharest, Splaiul Independentei 313, Bucharest, 060042, Romania*

^b*Mibatron SRL-Bucharest, Doamna Ghica 1, Bucharest, 022821, Romania*

^c*Department of Inorganic Chemistry, Physical Chemistry and Electrochemistry, University Politehnica of Bucharest, Calea Grivitei 132, Bucharest, 010737, Romania*

Why these types of ionic liquids?



□ A novel ionic liquid medium with interesting perspectives in metals and alloys electrodeposition has been recently developed, based on **choline chloride (2-hidroxy-ethyl-trimethyl ammonium chloride, vitamin B₄, ChCl) eutectic mixtures with different hydrogen bond donor compounds**, such as amides, glycols or carboxylic acids. These ionic liquids analogues proved to be cheap and easy to make, but they are environmentally friendly, too.

□ Detailed investigations are still required to implement these novel electrodeposition procedures, in order to optimize operation parameters and deposits characteristics. Additional information in this field may significantly contribute to the extension of the practical applications of these systems.

□ Metal and alloy composites with multiwall carbon nanotubes (**MWCNTs**) or graphene/graphene oxide (**GO**) related materials as coatings represent significant engineering materials suitable for a large range of industrial applications, due to their particular structures. The electrochemical route is of great interest for large scale manufacturing allowing the obtaining of various functional and protective composite coatings with lower cost and easier control of the process.

□ Therefore, some experimental results regarding the electrodeposition of **Co-MWCNTs, Ag-MWCNTs, Sn-rGO** and **Sn-Ni-rGO alloy** composites involving ChCl based electrolytes are presented. These media also facilitate the formation of stable and homogeneous dispersions of multiwall CNTs or graphene oxide nanosheets, thus overcoming the agglomeration problems.

- F. Endres, A.P. Abbott, D.R. MacFarlane (Eds), *Electrodeposition from Ionic Liquids*, Wiley-VCH Verlag, Weinheim, 2008.
- A.P. Abbott, G. Frisch, K.S. Ryder, *Electroplating using ionic liquids*, *Annual. Rev. Mater. Res.* 43 (2013) 335–358.
- Y. Zhang, X. Lu, X. Feng, Y. Shi, X. Ji, *Properties and applications of choline-based deep eutectic solvents*, *Progress in Chemistry* 26 (6) (2013) 881-892.
- M. Hayyan, et al., *Are Deep Eutectic Solvents Benign or Toxic?*, *Chemosphere*, 90(7) (2013) 2193-2195.
- E.L. Smith, A.P. Abbott, K.S. Ryder, *Deep eutectic solvents (DESs) and their applications*. *Chem. Rev.* 114 (2014) 11060–11082.
- M.L. Polo-Luque, et al., *Functionalization and dispersion of carbon nanotubes in ionic liquids*, *TrAC Trends in Analytical Chemistry* 47 (2013) 99-110.
- A. Abo-Hamad, M. Hayyan, M.A. AlSaadi, M.A. Hashim, *Potential applications of deep eutectic solvents in nanotechnology*, *Chem.Eng.J.* 273 (2015) 551-567.

1. Electrochemical deposition of Co-MWCNTs composites

Electrolyte: choline chloride – urea (1:2) eutectic mixture +1M CoCl_2 + (0.1-0.5)g/L multi-walled carbon nanotubes (MWCNTs). Good dispersion of CNTs (6.9 nm diameter, 5 μm length) by strong ultrasound stirring.

Establishing the conditions for composite electrodeposition

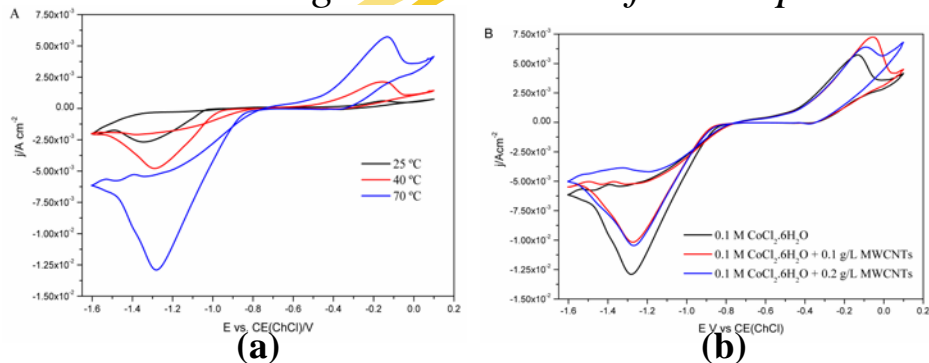


Fig. 1 CVs of Co-MWCNTs deposition on Cu substrate from ChCl-urea +1M CoCl_2 + (0.1-0.2)g/L MWCNTs, 5mV/s: (a) at different temperatures; (b) different concentration of MWCNTs at 70 °C.

The addition of MWCNTs has diminished the cathodic peak, but increased the anodic peak.

Characterization of Co-MWCNT coatings

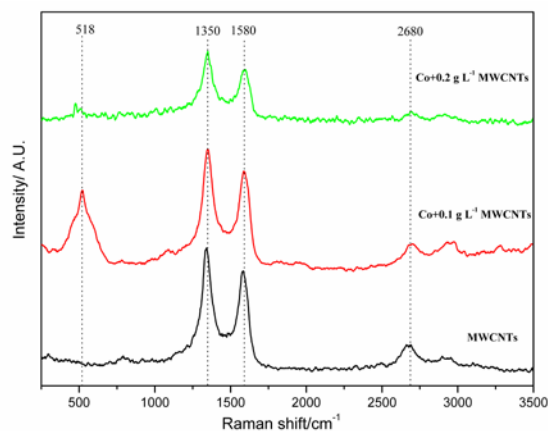
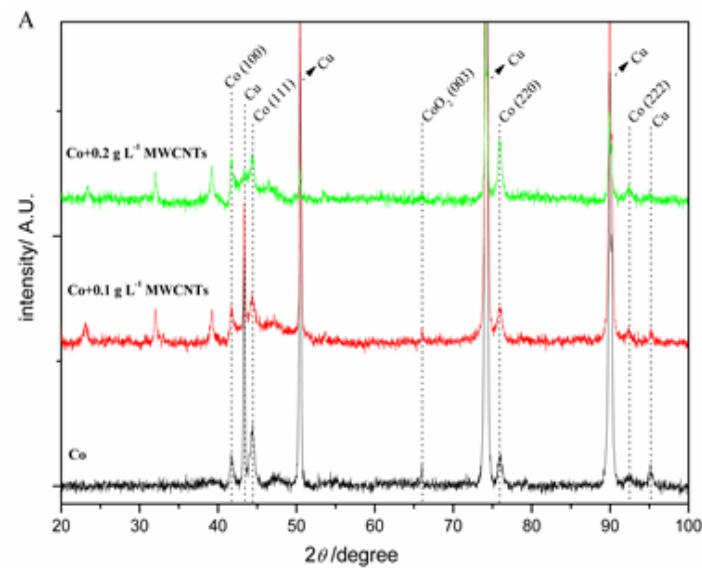


Fig. 2 Raman spectra for the MWCNTs (suspension in ChCl-urea) and Co-MWCNTs coatings prepared from ChCl-urea+1M CoCl_2 +0.1g/L MWCNTs ($i = 5\text{mA}/\text{cm}^2$, 15 min); ChCl-urea+1M CoCl_2 +0.2g/L MWCNTs ($i = 5\text{mA}/\text{cm}^2$, 15 min).

- Pure MWCNTs dissolved in ChCl-urea showed Raman bands at 1380, 1580 and 2666 cm^{-1} which are characteristic to the MWCNTs.
- Both cobalt containing samples gave also signals at Raman shifts assignable to MWCNTs, suggesting the successful formation of Co-MWCNTs composites.

- N.M. Pereira, O. Brincoveanu, A.G. Pantazi, C.M. Pereira, J.P. Araújo, A. F. Silva, M. Enachescu, L. Anicai, *Electrodeposition of Co and Co composites with carbon nanotubes using choline chloride-based ionic liquids*, *Surf. Coat. Technol.* DOI: 10.1016/j.surfcoat.2017.06.002
- M. Li, Z. Wang, R.G. Reddy, *Cobalt electrodeposition using urea and choline chloride*, *Electrochim. Acta* 123 (2014)325–331
- A. Cojocaru, M.L. Mares, P. Prioteasa, L. Anicai, T. Visan, *Study of electrode processes and deposition of cobalt thin films from ionic liquid analogues based on choline chloride*, *J. Solid State Electrochem.* 19 (4) (2015) 1001-1014.

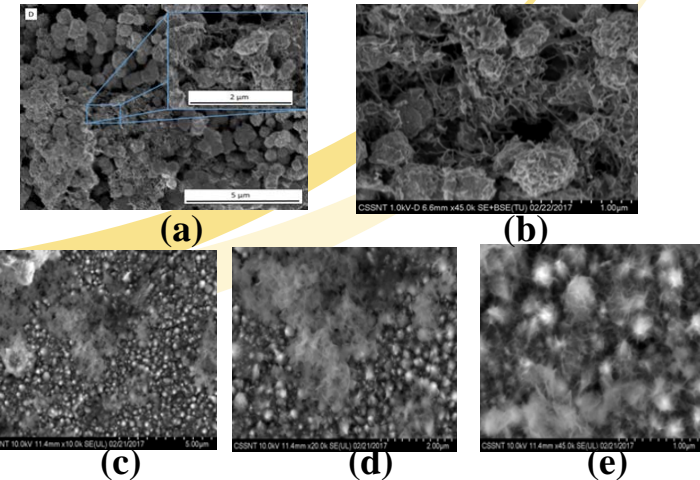
Fig. 3 X-ray diffractograms for **Co** and **Co-MWCNTs** composite coatings prepared ($i = 5 \text{ mA/cm}^2$, 15 min) from: **ChCl-urea+1M CoCl₂**; **ChCl-urea+1M CoCl₂+0.1 g/L MWCNTs**; **ChCl-urea+1M CoCl₂+0.2 g/L MWCNTs**.



- Literature shows that XRD patterns of MWCNTs evidence the strongest diffraction peak at the angle (2θ) of $\approx 25.5^\circ$, indexed as the (002) reflection of the hexagonal graphite structure. Existing differences for our Co-MWCNTs might be associated to deposit's internal stress and strain effects.
- Intensity of the peak assigned to Co(111) plane diminished and of Co(220) peak increased. This suggests that the presence of nanotubes promoted a preferential orientation of Co crystallites on (220).
- The inclusion of MWCNTs on the metal matrix modifies the grain dimensions and orientation.

Fig. 4 SEM images for the **Co+MWCNTs** prepared from **ChCl-urea+1M CoCl₂+0.2 g/L MWCNTs**:
(a,b) 6.6 mA/cm^2 , 30 min., approx. $2.5 \mu\text{m}$;
(c-e) 11 mA/cm^2 , 30 min., approx. $3.7 \mu\text{m}$.

- Co-MWCNTs films show different morphology from Co films, mainly consisting in relatively spherical particles connected by MWCNTs (incorporated nanotubes).
- They appear to be less compact as compared to pure cobalt.



• *S. Costovici, A.-C. Manea, T. Visan, L. Anicai, Investigation of Ni-Mo and Co-Mo alloys electrodeposition involving choline chloride based ionic liquids, Electrochim. Acta, 207 (2016) 97-111.*

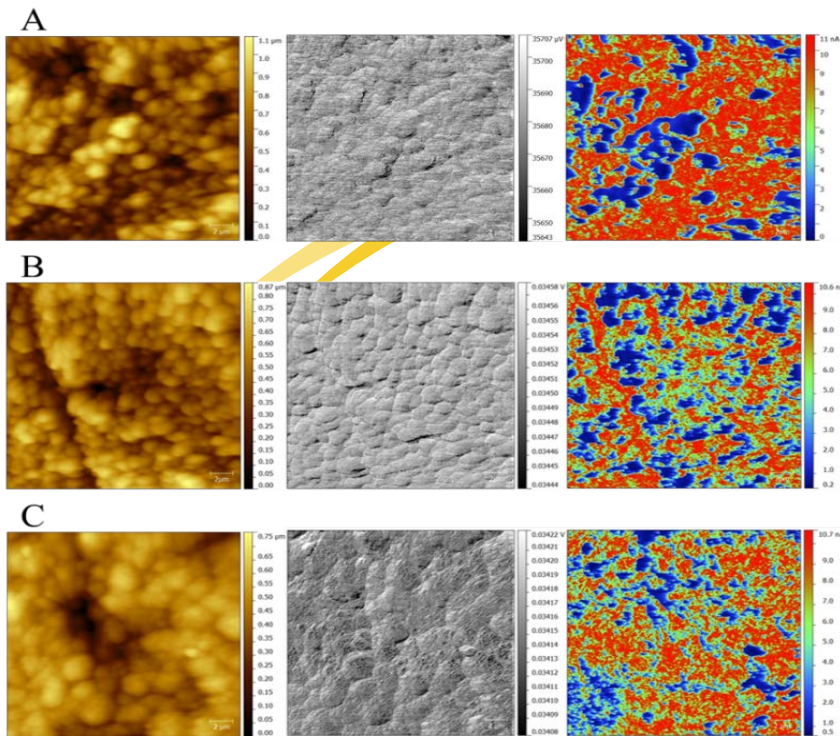


Fig. 5 AFM topographic images (a_1, b_1, c_1), friction images (a_2, b_2, c_2), and electrical conductivity maps (a_3, b_3, c_3 , bias voltage – 1V) ($20\mu\text{m} \times 20\mu\text{m}$) for **Co** and **Co-MWCNTs** coatings prepared from **ChCl-urea+1M CoCl₂ + (0.1-0.2)g/L MWCNTs** ($5\text{mA}/\text{cm}^2$, 15 min):
 (A) without MWCNTs;
 (B) +0.1g/L MWCNTs;
 (C) +0.2g/L MWCNTs.
 Surface of microarea: $20\mu\text{m} \times 20\mu\text{m}$

- The topography images show a surface formed by globular particles with diameters smaller than 600 nm. With such large height variations it is not possible to discern the nanotubes. Increasing the content of MWCNTs, the grains size diminished. Also, both average roughness (R_a) and the root mean square (RMS) roughness diminished as the amount of nanotubes in electrolyte increased.
- Friction force maps roughly show that the local friction coefficient varies from high friction regions (**bright**) to low friction regions (**dark**). The absence of contrasting regions (Fig. 5(a_2, b_2, c_2)) may suggest that the friction force varies slightly along the surface.
- Electrical conductivity varies from high conductivity zones (**red**) to low conductivity or high resistive zones (**blue**). The composites have slightly lower conductivity when compared with pure cobalt film. The presence of amorphous carbon in the MWCNTs and their random spatial distribution in addition to the presence of cobalt oxide in the deposited layer might explain this decrease.

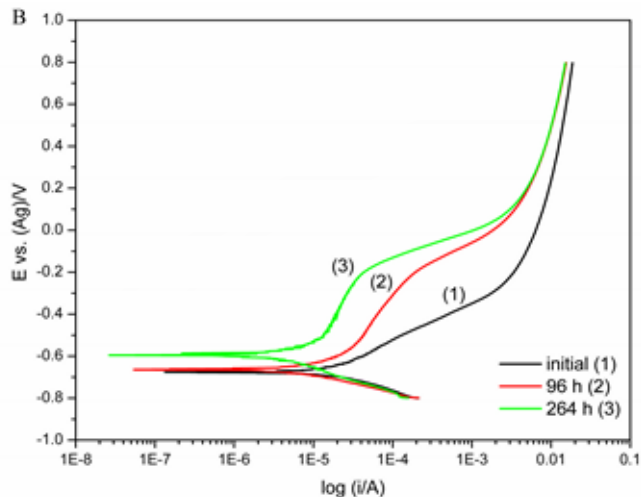
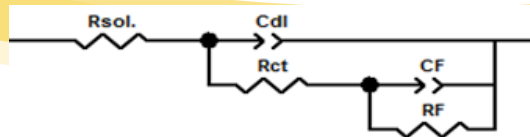


Fig. 6 Polarization curves (3mV/s) in 0.5M NaCl for **Co-MWCNTs** (prepared from ChCl-urea+1M CoCl₂+0.2g/L MWCNTs (*i*=6.6mA/cm², 30 min).

*i*_{corr} diminished as the immersion time increased which suggest the formation of a passive layer that improves the corrosion performance. Impedance plots evidence the presence of a single capacitive loop (Nyquist) and only one time constant in the middle frequency region (Bode).

Fig. 7 Equivalent-circuit proposed for **Co-MWCNTs** corrosion behavior in 0.5M NaCl aggressive solution.



- *N.M. Pereira, O. Brincoveanu, A.G. Pantazi, C.M. Pereira, J.P. Araújo, A. F. Silva, M. Enachescu, L. Anicai, Electrodeposition of Co and Co composites with carbon nanotubes using choline chloride-based ionic liquids, Surf. Coat. Technol. DOI: 10.1016/j.surfcoat.2017.06.002*
- *L. Anicai, S. Costovici, A. Cojocaru, A. Manea, T. Visan, Electrodeposition of Co and CoMo alloys coatings using choline chloride based ionic liquids - evaluation of corrosion behavior, Trans. Inst. Metal Finishing, 93 (6), 2015, 302-312.*

Table 1 Values of corrosion parameters from Tafel curves

Immersion time	Pure Co		Co-MWCNT	
	<i>E</i> _{corr} vs. Ag/V	<i>i</i> _{corr} /μA cm ⁻²	<i>E</i> _{corr} vs. Ag/V	<i>i</i> _{corr} /μA cm ⁻²
Initial	-0.690	7.23	-0.677	7.17
96 h	-0.642	7.07	-0.673	6.08
264 h	-0.587	3.23	-0.604	4.93

Table 2 Values of **R_{ct}** (charge-transfer resistance for electrolyte/passive film interface) and **R_F** (charge-transfer resistance for passive film / coating interface).

Immersion time	Pure Co		Co-MWCNT	
	R_{ct} (Ω cm ²)	R_F (Ω cm ²)	R_{ct} (Ω cm ²)	R_F (Ω cm ²)
Initial	458	8753	595	4200
24 h	10777	12536	224	4633
48 h	4235	5603	2403	5000
96 h	2454	1000	3650	10950
168 h	329	8840	4236	11500

2. Deposition of Ag-MWCNTs composite coating

Establishing the conditions for composite electrodeposition from *choline chloride-triethanolamine (IL-TEA) eutectic mixture*

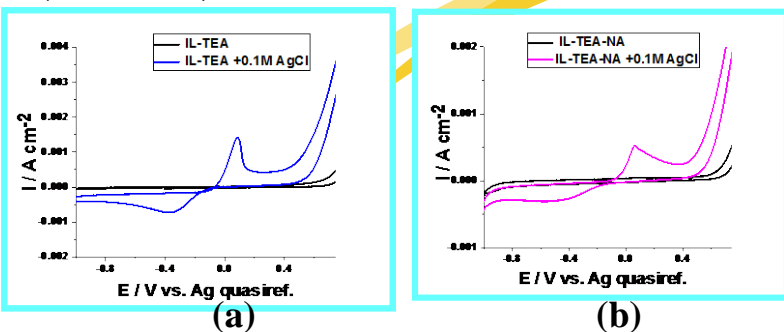


Fig. 8 Cyclic voltammograms of Ag^+/Ag couple in:
 (a) IL-TEA + 0.1M AgCl
 (b) IL-TEA + 0.1M AgCl + NA;
 GC working electrode, at 20mV/s, 70°C.

Table 3 Electrolyte compositions and operating parameters

Electrolysis conditions		Coating characteristics	
Ag-TEA	0.1M AgCl dissolved in IL-TEA (IL-TEA= choline chloride:triethanolamine (1:1))	1V, 70°C, 15-30 min., 300rpm magnetic stirring	Adherent, non-glossy grey-yellow, 0.3µm, 92.71-92,97 wt % Ag (EDX analysis)
Ag-MWCNTs	0.1M AgCl +2g/L MWCNTs suspensions in IL-TEA-NA (NA = 0.1M nicotinic acid)	3,5-4V, 2 mA/cm ² , 70°C, 15-30 min. with/whitout magnetic stirring	Adherent, non-glossy (matte) grey, 0.2-0.3µm, 93.40-94,29wt % Ag (EDX analysis)
Ag-MWCNTs	0.1M AgCl +2 g/L MWCNTs suspensions in IL-TEA-NA	Electrodeposition in ultrasonic bath, 8.5 V, 2 mA/cm ² , 70°C, 15-30 min	Adherent, non-glossy (matte) grey, 0.35-0.76 µm MWCNTs evidenced by SEM analysis
Ag-MWCNTs	0.1M AgCl +2 g/L MWCNTs suspensions in IL-TEA-NA	Electrodeposition in ultrasonic bath, 8.5 V, 4.8 mA/cm ² , 70°C, 15-30 min	Adherent, non-glossy (matte) grey, 0.25-0.35 µm MWCNTs evidenced by SEM analysis

A. P. Abbott, K. El Ttaib, G. Frisch, K. S. Ryder, D. Weston, *The electrodeposition of silver composites using deep eutectic solvents*, *Phys. Chem. Chem. Phys.* 14 (2012) 2443–2449.

P. Sebastián, E. Vallés, E. Gómez, *First stages of silver electrodeposition in a deep eutectic solvent. Comparative behavior in aqueous medium*, *Electrochim. Acta.* 112 (2013) 149–158.

Characterization of Ag-MWCNTs coatings

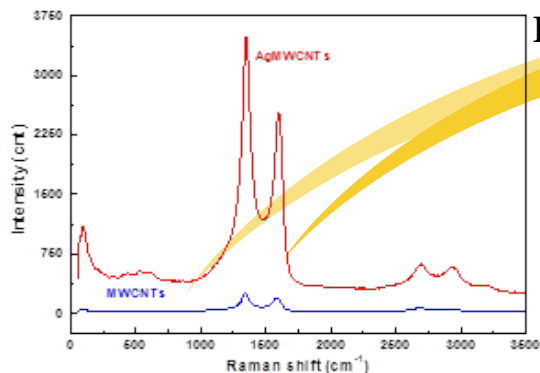


Fig. 9 Raman spectrum of Ag-MWCNTs coating (with green laser) prepared from 2g/L MWCNT s suspensions in IL-TEA-NA + 0.1M AgCl; 8.5 V, 4.8 mA/cm², 70°C, 15-30 min, ultrasound bath

- The presence of Raman bands characteristic to graphene: **D band** (1360 cm⁻¹) and **G band** (1593 cm⁻¹). The intensity of Raman bands increased with introduction of MWCNTs in coating, indicating a promising application for SERS measurements.
- The coatings morphology (SEM images) is in good agreement with the literature, but using aqueous electrolytes or other ionic liquids.

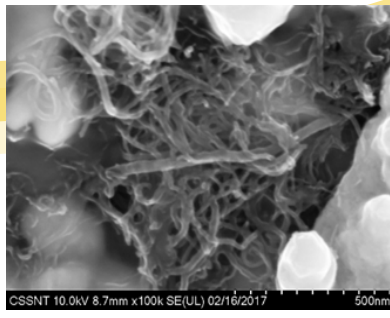
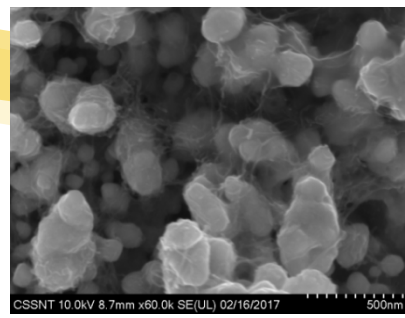
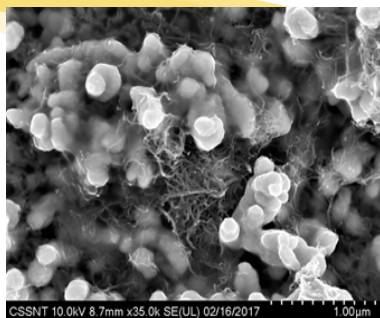
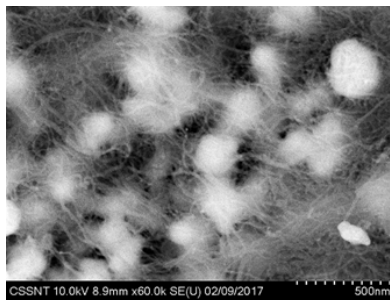
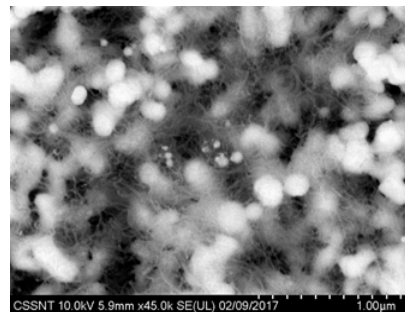
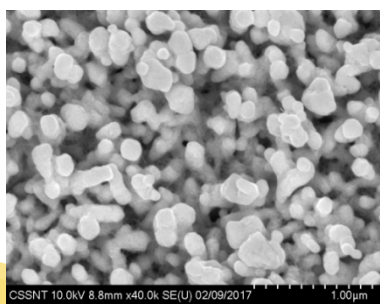


Fig. 10 SEM images of Ag-MWCNTs composites:
(a) 2g/L MWCNTs suspensions in IL-TEA-NA + 0.1M AgCl, 4V, 2 mA/cm², 70°C, 15-30 min, magnetic stirring.
(b) 2g/L MWCNTs suspensions in IL-TEA-NA + 0.1M AgCl, 8.5 V, 4.8 mA/cm², 70°C, 15-30 min, ultrasound bath.

- G. Dunieskys, M.E.H. Larrude, M. da Costa, F. Freire Jr., Synthesis and characterization of silver nanoparticle-multiwalled carbon nanotube composites, *J. Nanomaterials*, 2014, Article ID 654068, 7 pages

3. Deposition of Sn-rGO composite

Dispersion stability of graphene oxide nanosheets was excellent in the **choline chloride-ethylene glycol (ILEG)** eutectic solvent

Cyclic voltammetry (CV) of Sn^{2+}/Sn couple on GC electrode

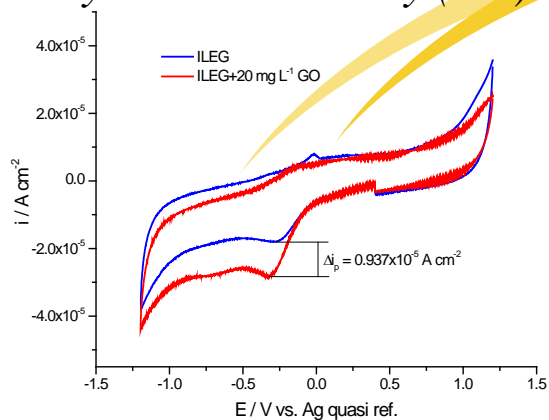


Fig. 11 CVs on GC for ILEG and ILEG+20mg/L GO, 25°C, 20 mV/s

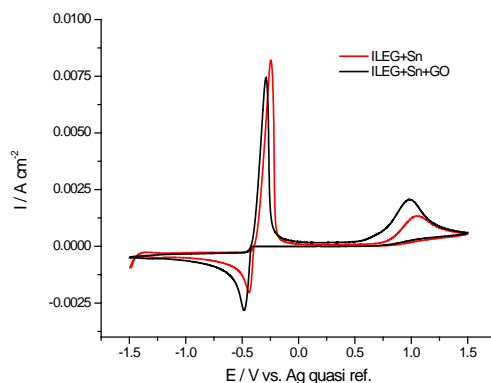


Fig. 12 Comparison of Sn and Sn+rGO deposition on GC from ILEG+50mM SnCl_2 and ILEG+50mM SnCl_2 +20mg/L GO, 25°C, 20 mV/s

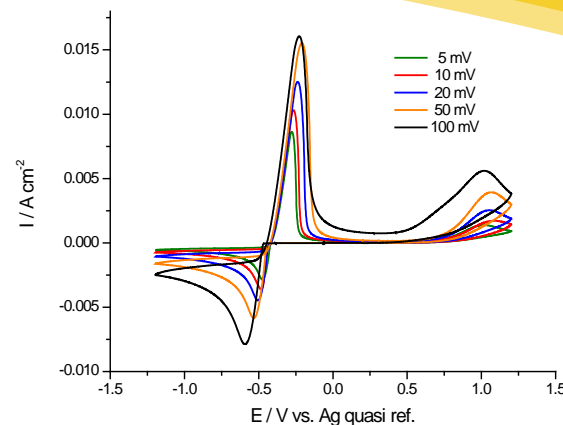


Fig. 13 Sn+rGO deposition on GC, from ILEG+50mM SnCl_2 +20mg/L GO, 25°C, different scan rates.

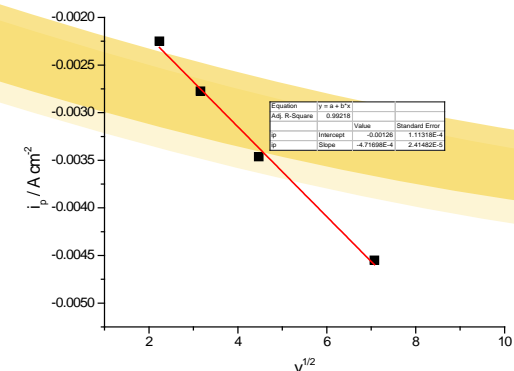


Fig. 14 Dependence of peak current density on scan rate for ILEG+50mM SnCl_2 +20mg/L GO

The experimental results show a diffusion-controlled cathodic process of **Sn-rGO** deposition from choline chloride – ethylene glycol + SnCl_2 + graphene oxide bath, at room temperature.

Table 4 Values of i_p from CVs with various scan rates (v) for ILEG+50mM SnCl_2 and ILEG+50mM SnCl_2 +20mg/L GO, 25°C

v (mV/s)	i_p (mA/cm ²)	
	ILEG +50 mM SnCl_2	ILEG+50mM SnCl_2 +20mg/L GO
5	2.25	2.83
10	2.77	3.61
20	3.46	4.47
50	4.55	5.82
100	4.85	7.89

Chronoamperometry study of nucleation for Sn+rGO deposits on GC electrode

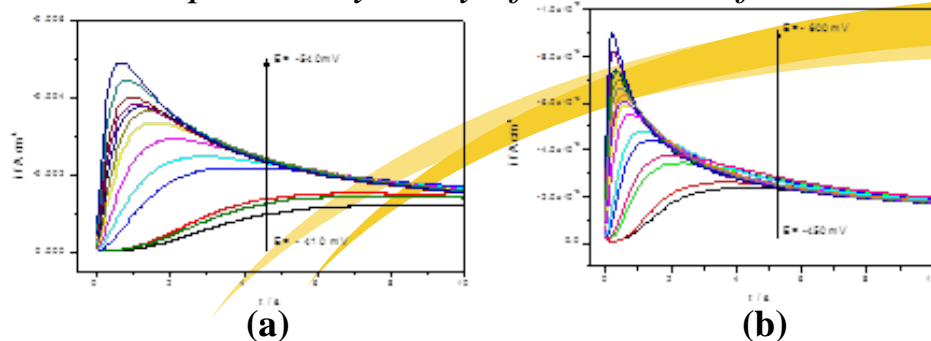


Fig. 14 Comparison of experimental current transients (i -time) for the nucleation of **Sn** from ILEG + 50mM SnCl₂, 25°C (a) and of **Sn-rGO** from ILEG + 50mM SnCl₂ + 20mg/L GO (b), 25°C; various potential steps.

We made a comparison of experimental data with theoretical curves ($i/i_{\max} - t/t_{\max}$) corresponding to instantaneous nucleation (eq.1) or progressive nucleation (eq.2) [Scharifker]:

$$(i_{\text{inst}}/i_m)^2 = 1.9542 \left\{ 1 - \exp[-1.2564(t/t_m)] \right\}^2 (t/t_m)^{-1} \quad (1)$$

$$(i_{\text{prog}}/i_m)^2 = 1.2254 \left\{ 1 - \exp[-2.3367(t/t_m)^2] \right\}^2 (t/t_m)^{-1} \quad (2)$$

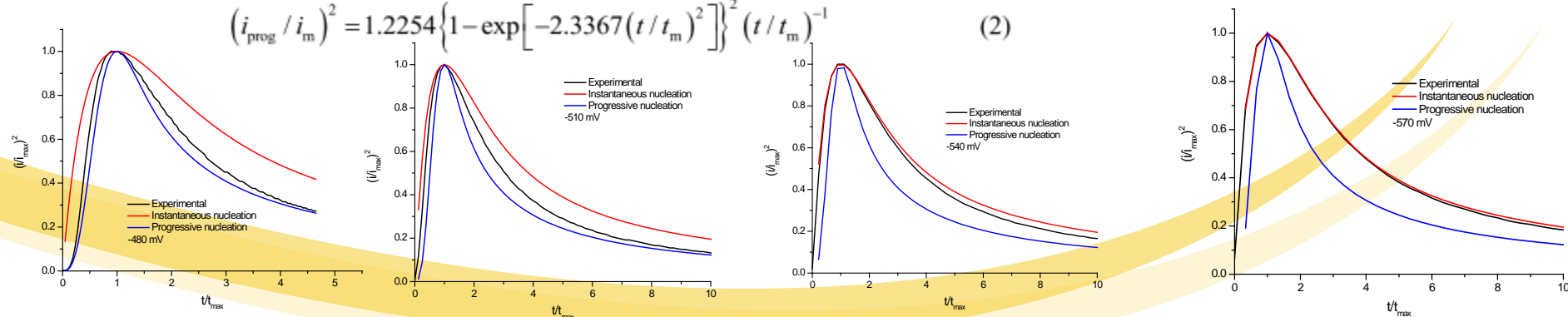


Fig. 15 Successive current transients for the nucleation of **Sn-rGO** showing gradual transition from progressive to instantaneous nucleation.

The time t_{\max} for **Sn-rGO** is shorter (from 4.3s to 0.2s) when the cathodic polarization increases.

The nucleation rate linearly increased [Ji] with the applied overpotential, having the slope higher than that for **Sn** coating.

- B.R. Scharifker, G.J. Hills, *Theoretical and experimental studies of multiple nucleation*, *Electrochim. Acta* 28 (1983) 879-889
- C. Ji, G. Oskam, P. Searson, *Electrochemical nucleation and growth of copper on Si(111)*, *Surface Science* 492 (2001) 115-124

Characterization of Sn-rGO composite coatings

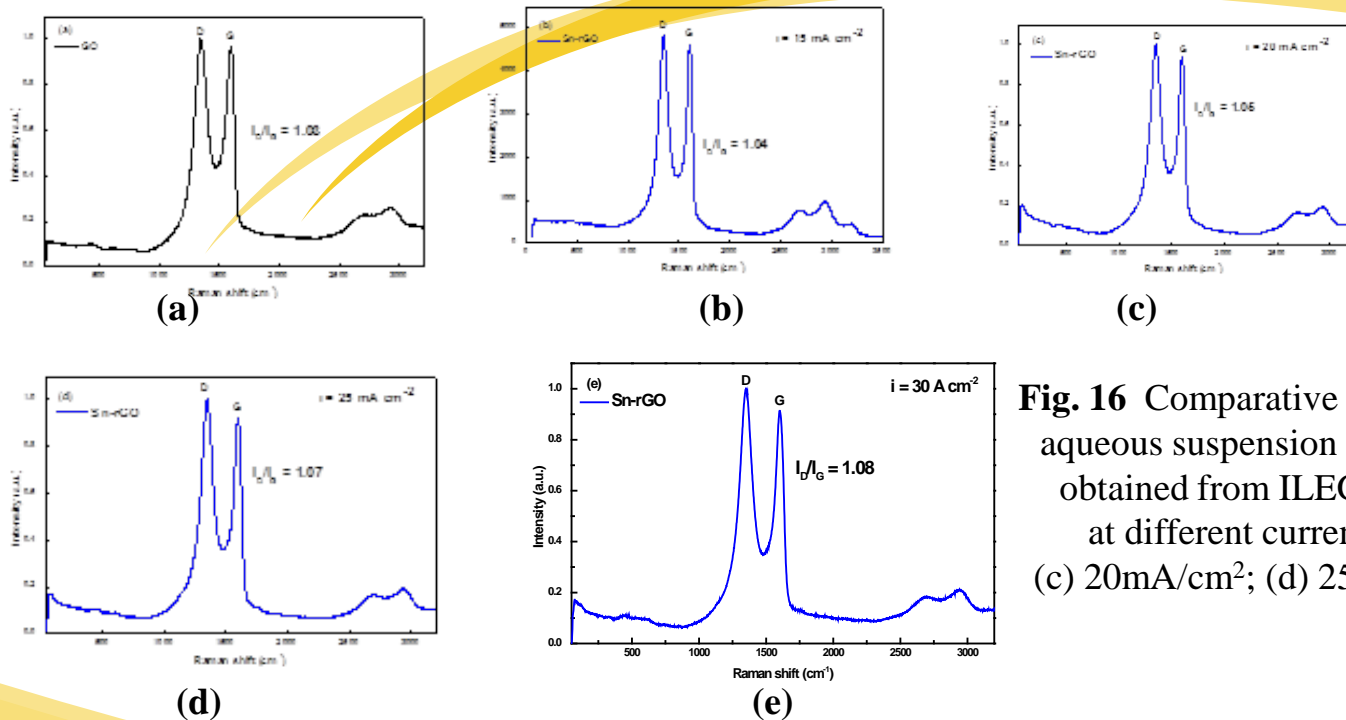


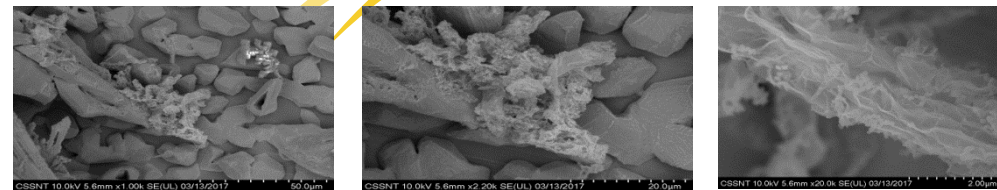
Fig. 16 Comparative Raman spectra of **GO** 1 mg/mL aqueous suspension **(a)** and **Sn-rGO (b-e)** coatings obtained from ILEG +0.7M SnCl₂ + 20mg/L GO at different current densities: **(b)** 15mA/cm²; **(c)** 20mA/cm²; **(d)** 25mA/cm²; **(e)** 30mA/cm²; 70°C.

- Two peaks at about 1361cm⁻¹ (**D band**, k-point phonons of A_{1g} symmetry) and 1584cm⁻¹ (**G band**, E_{2g} phonon of Csp² atoms) are observed. D/G intensity ratios in Sn-rGO coating are calculated to be 1.03-1.08.
- The increased D/G intensity ratio in Sn-rGO as compared to GO is due to a decrease in the average size of the sp² domains and an increase in the number of these domains, suggesting the reduction of GO to rGO in the electrodeposited composite [Wang, Feng].

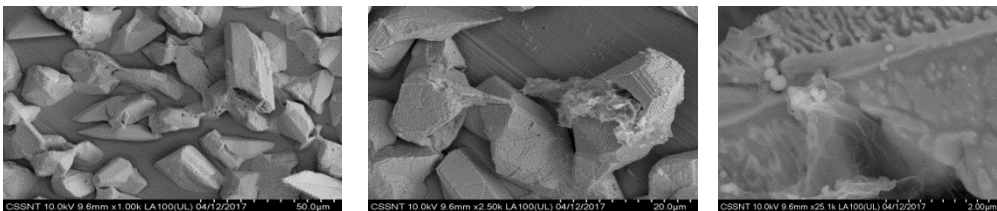
- G. Wang, B. Wang, X. Wang, J. Park, S. Dou, H. Ahn, K. Kim, Sn/graphene nanocomposite with 3D architecture for enhanced reversible lithium storage in lithium ion batteries, *J. Materials Chem.* 19 (2009) 8378-8384.
- B. Feng, J. Xie, G. Cao, T. Zhu, X. Zhao, Facile synthesis of ultrafine CoSn nanocrystals anchored on graphene by one-pot route and the improved electrochemical Li-storage properties, *New Journal of Chemistry* 37 (2013) 474.



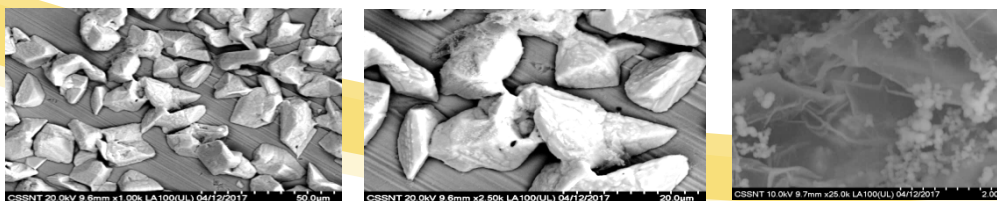
Sn, 15mA/cm², 30 min.



Sn-rGO, 15mA/cm², 30 min.



Sn-rGO, 20mA/cm², 30 min.



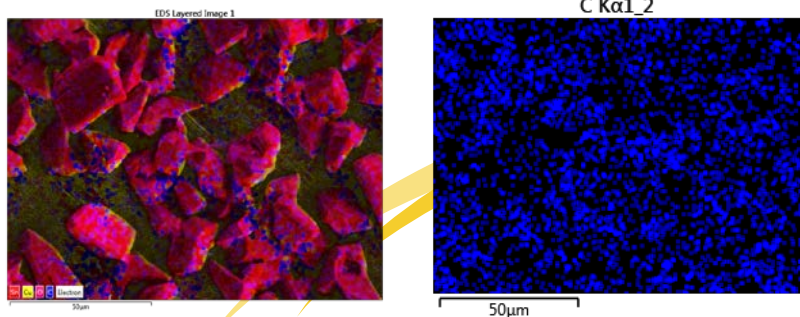
Sn-rGO, 25mA/cm², 30 min.



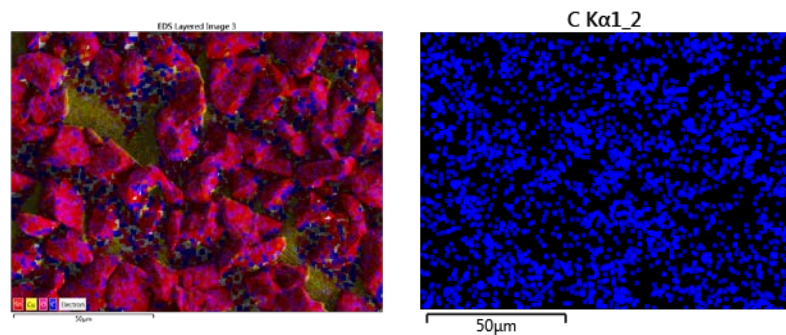
Sn-rGO, 30mA/cm², 30 min.

Fig. 17 Comparative SEM micrographs of **Sn** electrodeposited from ILEG + 0.7M SnCl₂ and **Sn-rGO** electrodeposited from ILEG +0.7M SnCl₂ + 20mg/L GO, different current densities; 70°C, magnetic stirring of bath.

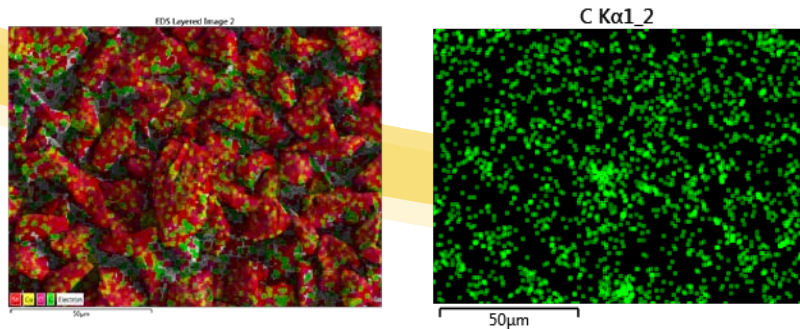
The recorded SEM micrographs showed that the rGO incorporation within the deposit needs current density values higher than 15 mA/cm², in agreement with [Salome et al.].



20 mA/cm²



25 mA/cm²



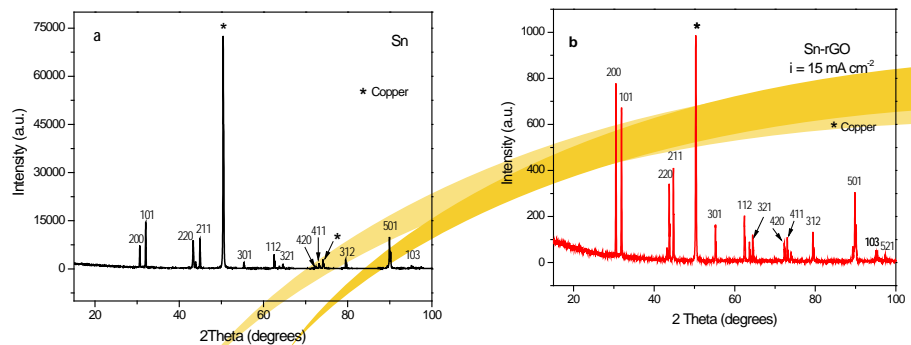
30 mA/cm²

Fig. 18 EDX mapping for **Sn-rGO** electrodeposited at different applied current densities (70°C, 30 min.)

Sn - red, Cu – yellow, O – purple (mouve),
C – dark blue or green.

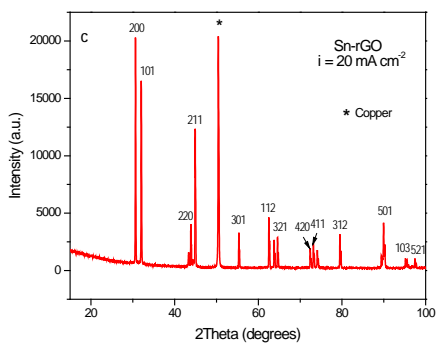
Energy dispersive X-ray diffraction analysis showed the presence of carbon uniformly distributed within the coating.

- S. Salomé, N.M. Pereira, E.S. Ferreira, C.M. Pereira, A.F. Silva, Tin electrodeposition from choline chloride based solvent: Influence of the hydrogen bond donors, *J. Electroanal. Chem.* 703 (2013) 80–87.

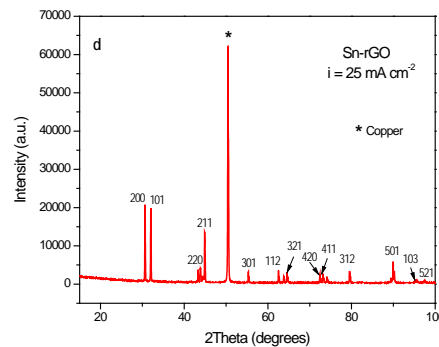


(a)

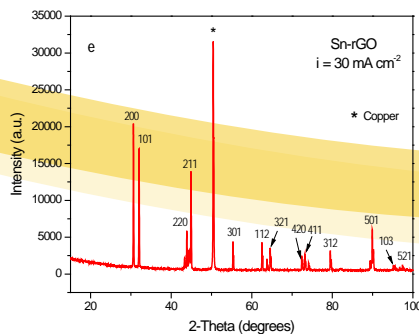
(b)



(c)



(d)



(e)

Fig. 19 Comparative X-ray diffractograms of Sn electrodeposited from ILEG + 0.7M SnCl₂ (a) and Sn-rGO electrodeposited from ILEG + 0.7M SnCl₂ + 20mg/L GO at different current densities: (a) 15mA/cm²; (b) 15mA/cm²; (c) 20mA/cm²; (d) 25 mA/cm²; (e) 30mA/cm².

- XRD patterns of Sn and Sn-rGO coatings show clearly the diffraction peaks of crystalline Sn nanoparticles. They can be indexed to the tetragonal Sn phase (S.G.: I41/amd(141)), indicating the crystalline nature of the Sn-rGO coating.
- The peak at $2\theta=23-28^\circ$ usually attributed to the graphene nanosheets is not prominent.

- L.P. Bérubé, G. L'Espérance, A quantitative method of determining the degree of texture of zinc electrodeposits, *J Electrochem Soc* 136 (1989) 2314-2315.

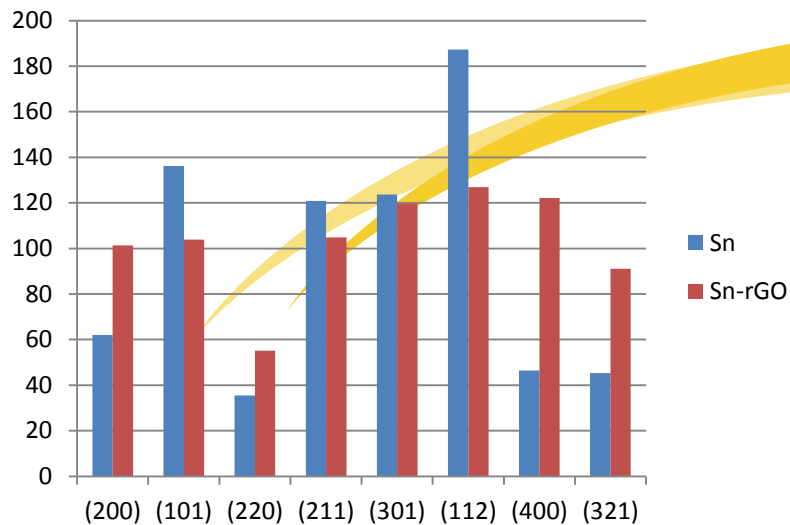


Fig. 20 Texture coefficients of Sn and Sn-rGO coatings for different planes

The preferred orientation of Sn and Sn-rGO was estimated from X-ray data according to the methodology developed by Berube and L'Esperance. The texture coefficient was calculated from the following equation:

$$Tc(hkl) = \frac{I(hkl)}{\sum I(hkl)} \times \frac{\sum I_o(hkl)}{I_o(hkl)} \times 100 \quad (3)$$

where: $I_{(hkl)}$ is the peak intensity of the electrodeposited Sn and I_o is the intensity of peak of standard Sn powder sample from JCPDS file card 004-0673.

Table 5 Texture coefficient of Sn and Sn-rGO coatings

Samples	2θ (degrees)	h k l plane	Crystallite size, (nm)	T _{c(hkl)}
Sn coating	30.63	200	77.9	62.01
	32.01	101	78.5	136.14
	43.87	220	84.8	35.51
	44.90	211	85.4	120.93
Sn-rGO coating I _c = 20 mAcm ⁻²	30.63	200	76.4	101.35
	31.99	101	76.5	103.91
	43.83	220	78.5	55.19
	44.90	211	78.5	104.91

- The average sizes of cristallites have been estimated to be around 81 nm for Sn and 77 nm for Sn-rGO deposits using Debye-Sherrer' equation regardless the applied current density.
- A more pronounced orientation along the planes (101), (211), (301) and (112) has been noticed in the case of pure Sn, while the presence of rGO in the deposit diminished this tendency.

- L.P. Bérubé, G. L'Esperance, A quantitative method of determining the degree of texture of zinc electrodeposits, J. Electrochem. Soc. 136 (1989) 2314-2315.

4. Electrochemical deposition of Sn-Ni + rGO composite alloys

Applications of Sn-Ni: as soldering alloys [Liu] and as electrodes in Li-ion batteries [Yang]

Sn-Ni-rGO composite coatings (1 μ m) were obtained applying current densities in the range of 30-80 mA/cm² for 30 min. under stationary conditions or ultrasound stirring, at temperatures between 30-50°C.

The electrolyte: **choline chloride-ethylene glycol eutectic mixture** (denoted ILEG) + (0.1-2)M total concentrations of (**SnCl₂+NiCl₂**) + 1-2 g/L GO.

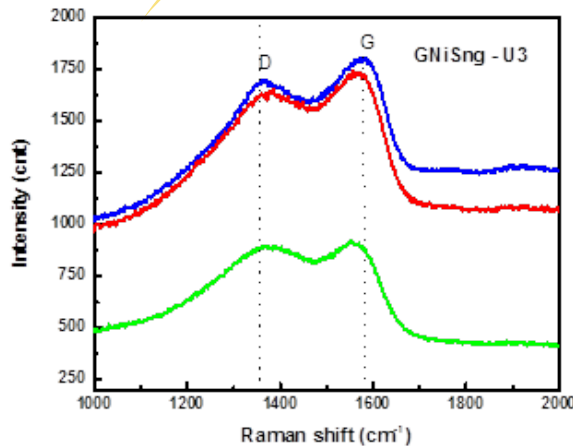


Fig. 21 Raman spectra of **Sn-Ni-rGO** composite alloys prepared under various hydrodynamic conditions (stationary or ultrasound stirring).

- The Raman bands characteristic to graphene: **D band** (1360 cm⁻¹) and **G band** (1593 cm⁻¹) were noticed [Jiang].
- Adherent, uniform **Sn-Ni-rGO** composite coatings have been electrodeposited.
- According to the literature, the electrochemical reduction of **GO** to **rGO** takes place simultaneously with the alloy deposition.

- X.D. Liu, Y.D. Han, H.Y. Jing, J. Wei, L.Y. Xu, *Effect of graphene nanosheets reinforcement on the performance of Sn-Ag-Cu lead-free solder*, *Mater. Sci. Eng. A* 562 (2013) 25–32.
- H. Yang, L. Li, *Tin-indium/graphene with enhanced initial coulombic efficiency and rate performance for lithium ion batteries*, *J. Alloys Compd.* 584 (2014) 76–80.
- Y. Jiang, T. Yuan, W. Sun, M. Yan, *Electrostatic spray deposition of porous SnO₂/graphene anode films and their enhanced lithium-storage properties*, *ACS Appl. Mater. Interfaces* 4 (2012) 6216–6220.
- A. Cojocaru, S. Costovici, L. Anicai, T. Visan, P. Cojocaru, L. Magagnin, P.L. Cavallotti, *Tin-nickel alloy deposition from choline chloride-urea ionic liquids (Deposizione di una lega nichel-stagno da soluzioni ioniche a base di cloruro di colina-urea)*, *Galvanotecnica e nuove finiture*, No. 3, (2009) 140-146.
- L. Anicai, A. Petica, S. Costovici, P. Prioteasa, T. Visan, *Electrodeposition of Sn and NiSn alloys coatings using choline chloride based ionic liquids—Evaluation of corrosion behavior*, *Electrochim. Acta* 114 (2013) 868–877.

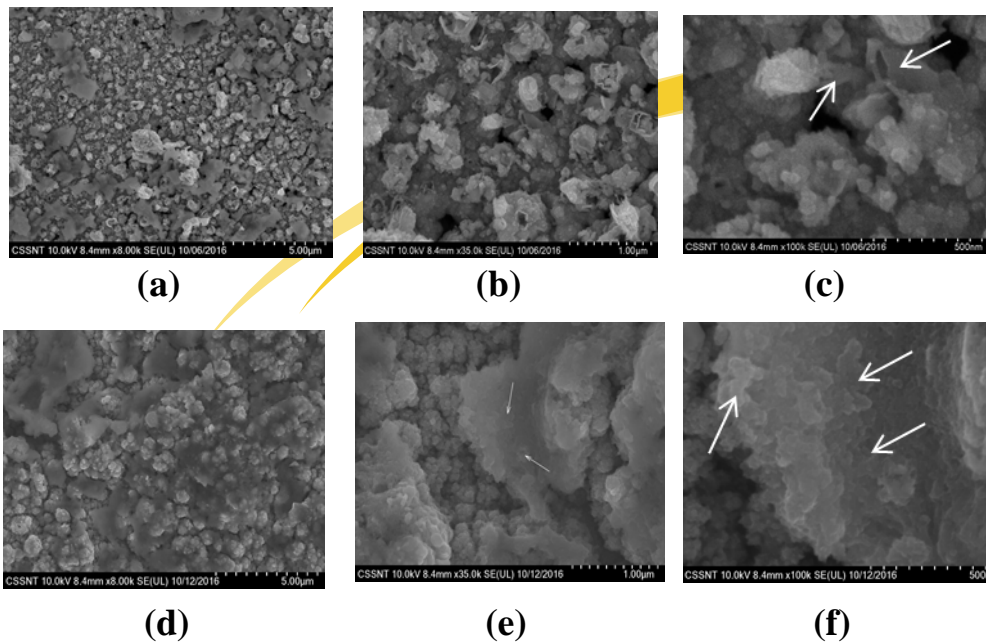


Fig. 22 SEM images of **Sn-Ni-rGO** composite alloys prepared at 50°C, from:
(a-c) ILEG + 67mM SnCl₂ + 33mM NiCl₂ + 2g/L GO, 50 mA/cm², 30 min.;
(d-f) ILEG + 0.25M SnCl₂+ 0.25M NiCl₂ + 2g/L GO, 30 min., ultrasound stirring.

- Adherent, uniform **Sn-Ni-rGO** composite coatings have been electrodeposited.
- The composite coatings contained about 67-70% Sn according to EDX analysis, with a very slight variation against the applied current density domain.
- The additional application of ultrasonic stirring of the electrolyte significantly increased the layer thickness of the deposited composite up to 10-12 μm at 30-40 mA/cm² for 30 min.
- Preliminary XRD studies showed that addition of graphene oxide in Sn-Ni alloy matrix determined a decrease in the grain sizes. The XRD patterns (not shown here) exhibited a diffraction peak at around 25°, however of a lower intensity as compared to other peaks.
- According to XRD patterns, the electrochemical deposited **Sn-Ni-rGO** composite coatings show a nanocrystalline structure, with average sizes of the cristallites around 11-14.5 nm.

Concluding remarks

- Co-MWCNTs, Ag-MWCNTs, Sn-rGO and Sn-Ni-rGO composite alloys have been successfully electrodeposited from choline chloride based ionic liquids analogues.
- Preliminary investigations (generally involving electrochemical techniques) allowed us to optimize the operating parameters for composites electrodeposition.
- The physical characterization of composite coatings using Raman spectroscopy, SEM (AFM) microscopy and XRD confirmed the incorporation of CNTs and graphene oxide nanosheets (GO), respectively. For composite alloys containing graphene oxide the electrochemical reduction of GO to rGO is supposed to take place during the cathodic process.
- Raman spectra exhibit specific bands for the corresponding MWCNTs or GO species. In addition, the recorded Raman spectra in the case of Ag-MWCNTs composites suggest their application for SERS analysis.
- The SEM microscopy evidenced the presence of the involved carbon nanomaterial incorporated within the metallic deposit.
- The recorded XRD patterns showed that the MWCNTs or rGO presence within the metallic matrix modifies the grain orientation and diminishes the grain sizes of the metallic species.

Acknowledgements

Part of this work was supported by the Romanian Ministry of Education,
EXECUTIVE AGENCY FOR HIGHER EDUCATION, RESEARCH, DEVELOPMENT
AND INNOVATION FUNDING,
under **NANOCOATIL** project 7-082/2013 and **NOVTINALBEST** project 38/2016,
both from **M Era Net Program**

The slide features two thick, curved yellow lines that sweep across the top and bottom of the page, framing the central text. The top line starts on the left and curves towards the right, while the bottom line starts on the left and curves towards the right, mirroring the top line's shape.

Thank you very much for your attention !