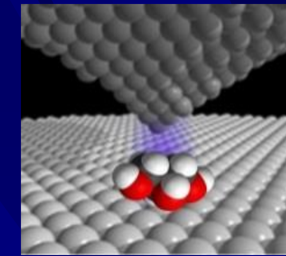


ALUMINUM SURFACE TREATMENTS INVOLVING DEEP EUTECTIC SOLVENT FORMULATIONS

<u>Liana Anicai</u>, Adrian-Cristian Manea, Andreea Florea, Oana Brincoveanu, Aida Ghiulnare Apaz, Marius Enachescu

POLITEHNICA University of Bucharest, Center of Surface Science and Nanotechnology, Splaiul Independentei nr. 313, Bucharest, 060042, Romania

WHY THESE TYPES OF IONIC LIQUIDS?

- An ionic medium with interesting perspectives in metals electrochemical surface treatment is that based on the so-called ***„deep eutectic solvents“ (DES)***, consisting in eutectic mixtures of quaternary ammonium salt such as choline chloride (2-hidroxy-ethyl-trimethyl ammonium chloride) with a hydrogen bond donor species such as amides, glycols or carboxylic acids. They are potentially recyclable, biodegradable and with no harm on human health.

- Despite of the growing interest in the field of “tailor-made” inorganic materials production, very few works were devoted to ***the effect of DES on valve metals anodic behaviour and on the morphology of the obtained oxide nanostructures***. *Additional information in this field* may significantly contribute to the extension of the practical applications of these systems.

- With this in view, some preliminary ***experimental results regarding the anodic behavior of Al substrate in various choline chloride based ionic liquids to produce either high quality polished surfaces or anodic oxide layers, are presented.***

CONTENTS

Al anodic surface treatments involving DES based electrolytes

Electrochemical polishing

Electropolishing operating parameters and the appearance of the modified Al surface

Anodic oxidation

- *Aspects regarding anodic behaviour of Al electrode in DESs based electrolytes*
- *Anodization process – operation parameters, anodic layers physical-chemical characterization*

EXPERIMENTAL

Electrochemical polishing

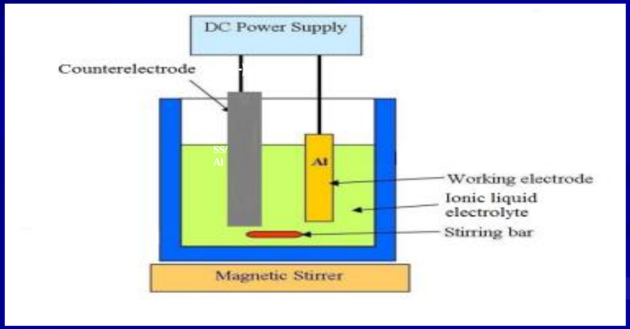
Aspects regarding electrochemical investigations through cyclic voltammetry and chronoamperometry

Anodic oxidation

Physical-chemical and structural characterization

Ionic liquid systems used for Al anodic surface treatments

System type	Electrolyte composition
Electropolishing	
ILEG	ChCl:EG 1:2 molar ratio
ILEG -OxAc	ILEG + 3% oxalic acid
ILEG-$VOSO_4$	ILEG +2% $VOSO_4$
IL	ChCl:urea 1:2 molar ratio
IL-NH_4NO_3	IL + 50 g/L NH_4NO_3
IL-OxAc	IL + 3% oxalic acid
Anodization	
ILGly	ChCl: glycerol 1:2 molar ratio
ILOx	ChCl: Oxalic acid 1:1 molar ratio
ChCitOx	Choline citrate: Oxalic acid 1:1 molar ratio
ChCitOx-IsOH-EG	ChCitOx:Isopropilic alcohol:Ethylene glycol 20:20:10 (volumic ratio)



- *Cyclic voltammogramms → at sweep rates of 10-50 mV/s, using a Al WE (S = 0.19 cm^2), against Ag wire as quasi-reference electrode and a Pt counterelectrode.; Cronoamperometric measurements (I-t curves) → for different applied voltages between 2 – 10 V, involving the same three-electrode cell. An Autolab PGSTAT 12 potentiostat controlled with GPES software as electrochemical equipment has been used. Dielectric properties of the obtained anodic films, involving EIS .*
- *AFM analysis (tapping mode, ambient atmosphere, using an AFM Solver Next equipment from NT-MDT)*

RESULTS AND DISCUSSION

Aluminum electrochemical polishing

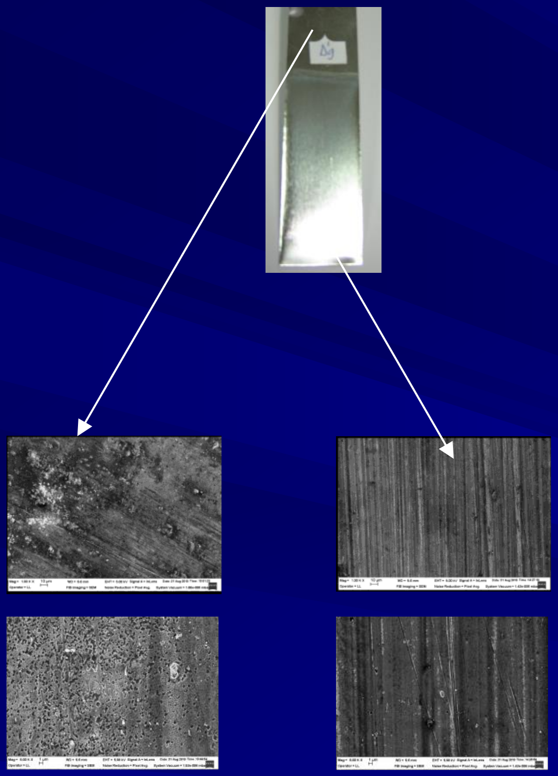
Electropolishing operating parameters and the appearance of the modified Al surface

IL type	Al substrate type	Current density, A/dm^2	Temperature, ^oC	Time, min.	Surface Appearance
ILEG	Al strip	5	7-8	6	Bright
		10	7-8	6	Smoothed, dull
ILEG-OxAc	Al strip	**4**	**14**	**6**	**Very bright**
		8	27	0.5-1	Dull
	Al foil	**3.3-4**	**3-17**	**5-10**	**Bright**
ILEG-$VOSO_4$	Al strip	4	3-14	10	Bright
	Al foil	3.3	20-30	15	Bright
		15	40-50	7	Surface leveling, uneven bright
IL	Al strip	4-6	45-85	5-6	Etched surface
IL-OxAc	Al strip	3-3.5	70-90	5-10	Surface leveling, dull
		2-2.5 (constant voltage)	70	10-20	Bright
IL-NH_4NO_3	Al strip Al foil	**10-15 (8 V, constant voltage**	**50**	**15**	**Bright**

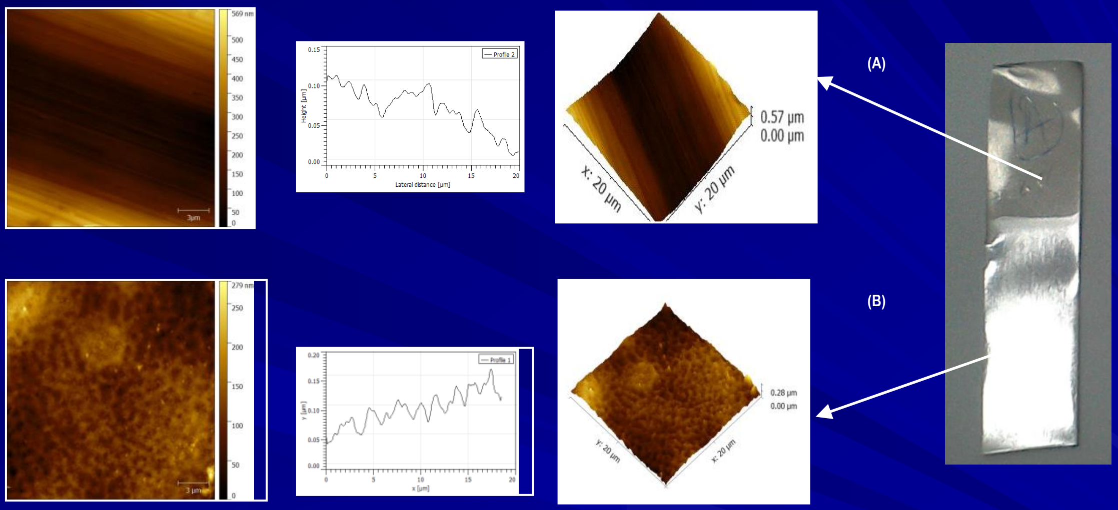
Higher values of the applied current density usually determine the formation of a smooth, but dull surface. Generally, ILEG based systems produce bright surfaces at temperatures in the range 3-30^{o}C. On the contrary, the use of IL based baths yielded a shiny appearance when higher temperatures are applied, respectively of minimum 50^{o}C. In addition, the IL based electrolytes work better under constant voltage conditions.

RESULTS AND DISCUSSION

Aluminum electrochemical polishing



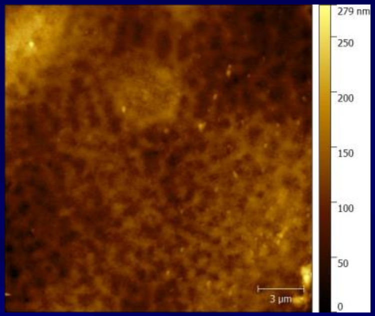
Comparative SEM micrographs of electropolished Al using ILEG-OxAc system at 5 ^{o}C, 5 min. 4 A/dm^2 (right) and of bare Al (left) surfaces



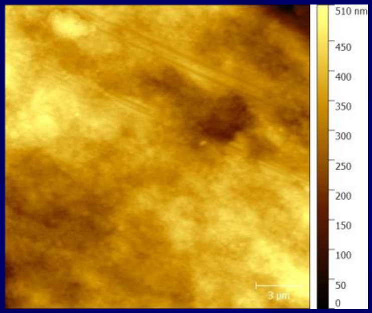
Comparative 2D and 3D AFM images and profiles of electropolished Al using IL-NH_4NO_3 system at 8V, 50^{o}C for 15 min. (B) and of bare Al (A) surface

RESULTS AND DISCUSSION

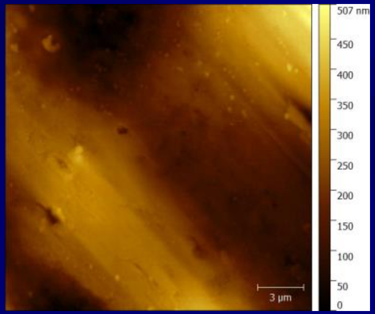
Aluminum electrochemical polishing



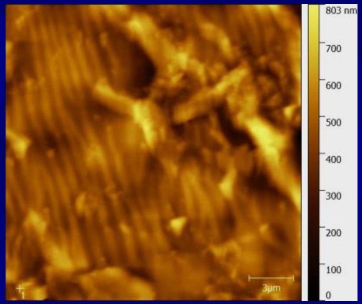
8V / 50^{o}C / 15 min.



15V / 50 ^{o}C / 15 min.



8V / 50^{o}C / 30 min.



8V / 80^{o} C / 15 min.

2D AFM images of different topographies formed on the surface of electropolished Al after electropolishing in IL-NH_4NO_3 system for various durations of time, at various voltages and temperatures

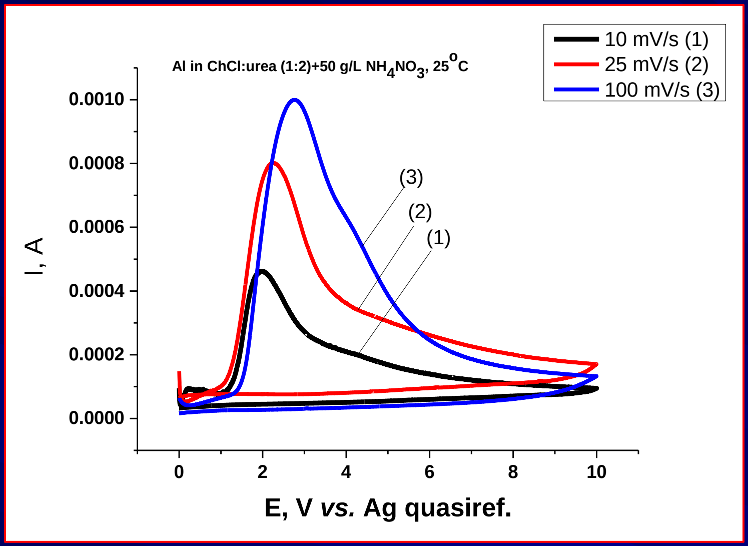
The influence of Al electropolishing operating parameters on the surface roughness parameter - investigation areas of 20x20 μm

Electropolishing conditions	RMS roughness, nm
untreated	101.97
15 V, 50^{o}C, 15 min.	67.82
8V, 80^{o}C, 15 min.	83.89
8V, 50^{o}C, 30 min.	90.03
8V, 50^{o}C, 15 min.	**30.12**

- The surface morphology of the Al surface after EP revealed the formation of various topographies, i.e. low ordered cellular patterns (8V, 50^{o}C, 15 min.), stripes (8V, 80^{o}C, 15 min.) or dimples (15 V, 50^{o}C, 15 min.)
- Higher temperatures and durations facilitated an increase of roughness, due to a stronger non-homogeneous etch of the surface. Voltages above 8V yielded also higher RMS roughness results.

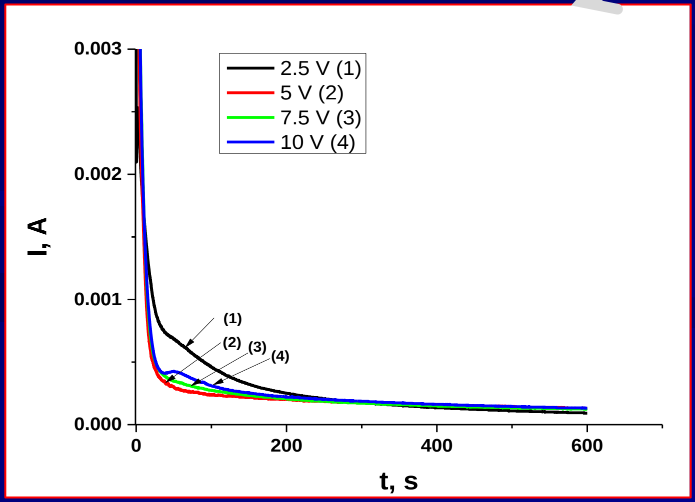
RESULTS AND DISCUSSION

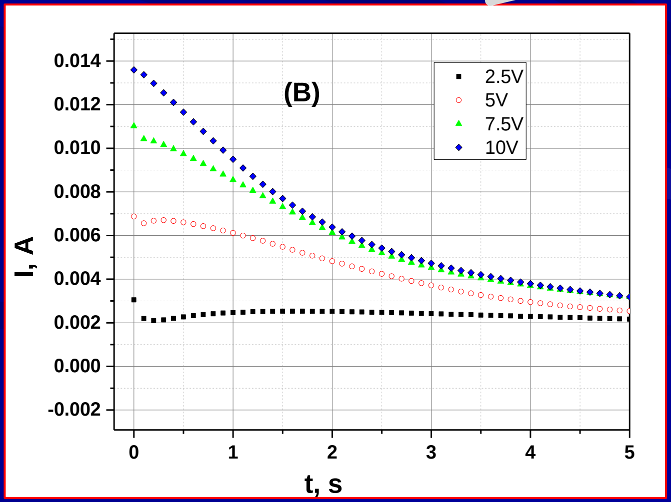
Aluminum electrochemical polishing



Cyclic voltammograms recorded in IL-NH_4NO_3 electrolyte for Al WE at 25°C at different scan rates (S_{WE}(Al) = 0.19 cm^2)

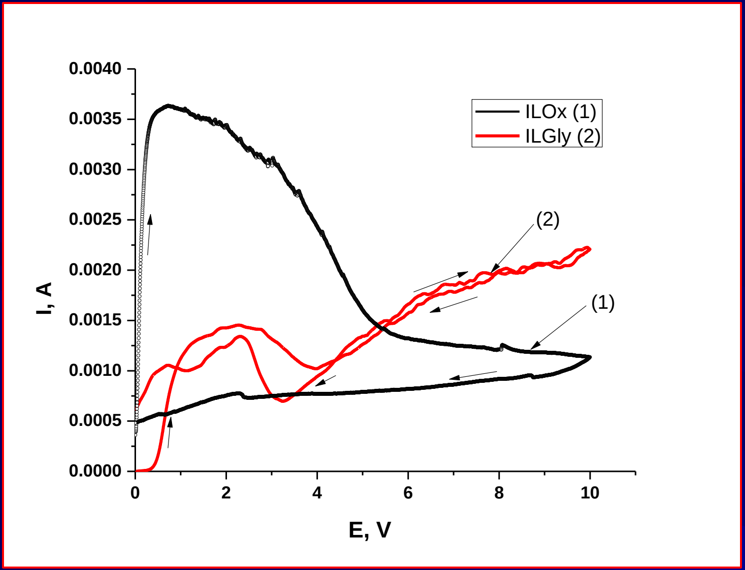
Current transients during the potentiostatic polarization of Al electrode (S = 0.19 cm^2) at different values of the applied potential in IL-NH_4NO_3 electrolyte for: (A) 600 s; (B) magnification of the starting region to evidence the initial moment characteristics



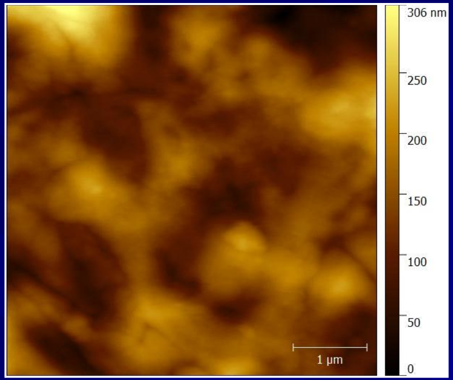


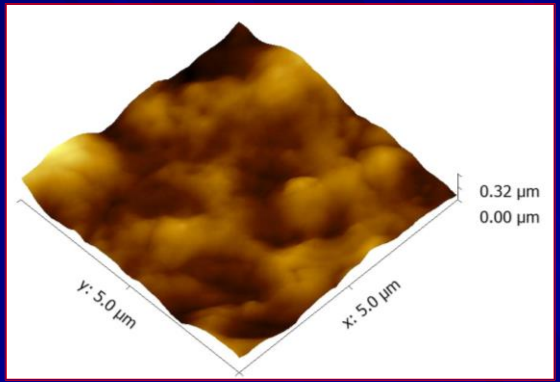
RESULTS AND DISCUSSION

Aluminum anodization



Cyclic voltammograms for Al working electrode ($0.19\ cm^2$) in: (1) ILOx and (2) ILGly electrolytes (Scanning rate: $25\ mV\ s^{-1}$)





2D and 3D AFM images of anodic alumina using ILGly, at a constant voltage of 30V, for 20 min., at 25°C

The use of ChCl based systems determines the formation of a rather etched surface, due to the presence of Cl^- anion. Thin oxide layers are formed, with an anodization rate of about 0.02 μm/min.

To minimize the influence of halide anion (in our case Cl^-) and form thicker anodic oxide layers, <u>choline dihydrogen citrate has been selected to prepare the eutectic mixtures as anodization electrolytes.</u>

RESULTS AND DISCUSSION

Aluminum anodization

Nanoporous anodic alumina layers involving choline dihydrogen citrate based eutectic mixtures

ChCitOx
↓
Choline citrate: Oxalic acid 1:1 molar ratio

ChCitOx-IsOH-EG
↓
ChCitOx:Isopropilic alcohol:Ethylene glycol 20:20:10 (volumic ratio)

- Viscosity: 300-25 mPa·s for temperatures between 40-80°C, with the highest values in the case of ChCitOx system;
- Electrical conductivity for temperatures between 25 and 80°C :
  - 0.03 – 0.73 mS cm^{-1} (ChCitOx);
  - 0.6-4 mS cm^{-1} (ChCitOx-IsOH-EG)

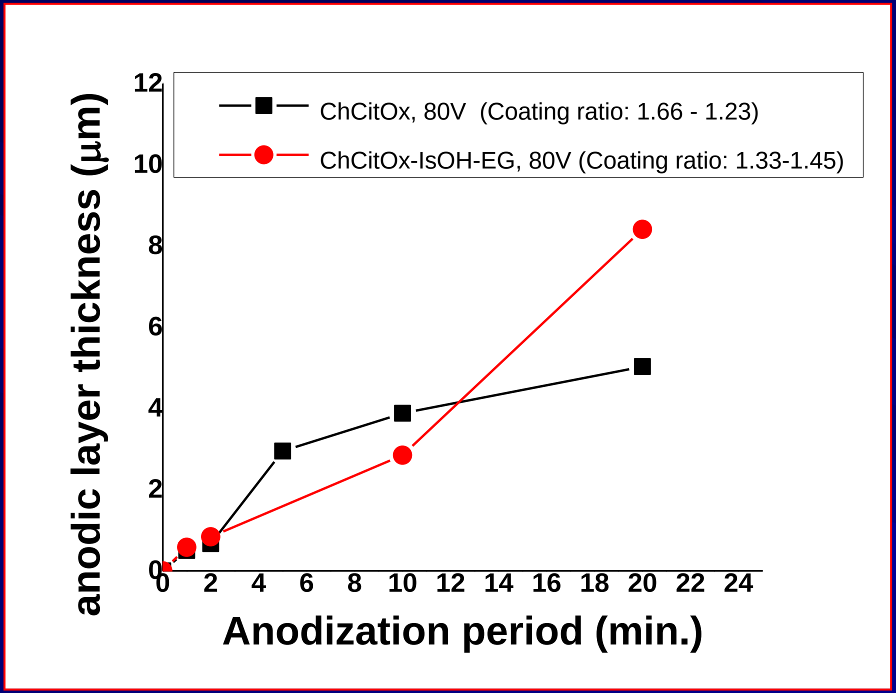
Due to the relatively high viscosity of the investigated electrolytes, the anodization process has been conducted at temperatures of 40-75°C, either at constant voltage or at constant current density.

Photographic images of anodic alumina films obtained in:
(a) ChCitOx electrolyte for 20 min. and
(b) ChCitOx –IsOH-EG electrolyte for 60 min. (60°C, 80 V)

RESULTS AND DISCUSSION

Aluminum anodization

Nanoporous anodic alumina layers involving choline dihydrogen citrate based eutectic mixtures



Dependence of anodic alumina layer thickness against anodization duration using ChCitOx and ChCitOx-IsOH-EG electrolytes

An anodization rate of about 0.41 µm/min. has been determined in the case of ChCitOx–IsOH-EG electrolyte, while two linear regions were noticed in the case of ChCitOx system, materialized by different anodization rates, of 0.6 µm/min. for the first 5 min., respectively of 0.13 µm/min. for longer periods. This behavior may be related to the high viscosity of the eutectic mixture.

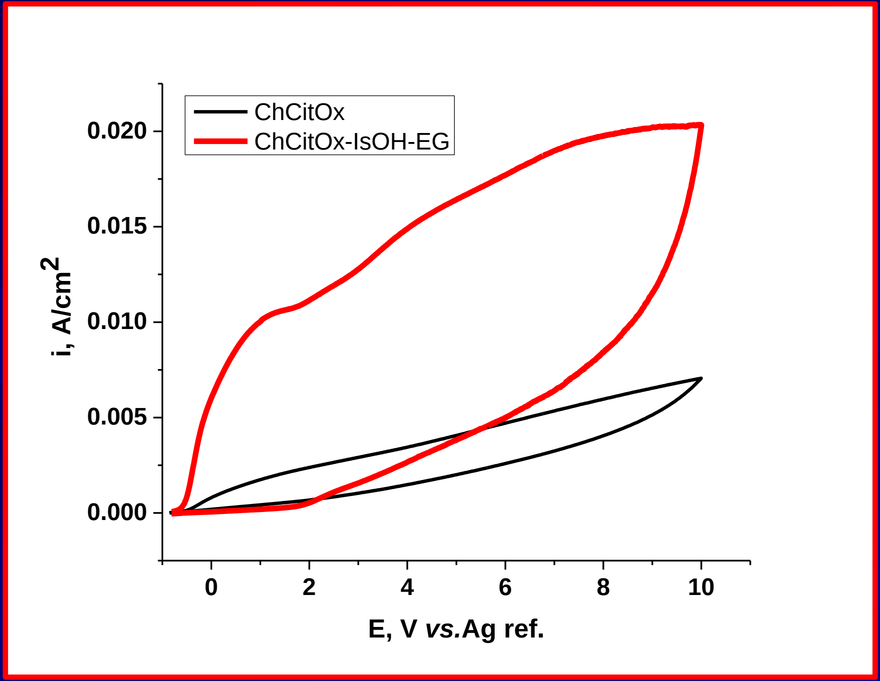
Anodic efficiencies: 65-87%, slightly higher than those obtained during anodization in classical aqueous acid electrolytes.

The novel electrolytes based on ionic liquid systems allow the operation at relatively high values of the temperature, in the range of 45-70°C with no significant decrease of the anodization rate.

RESULTS AND DISCUSSION

Aluminum anodization

Nanoporous anodic alumina layers involving choline dihydrogen citrate based eutectic mixtures

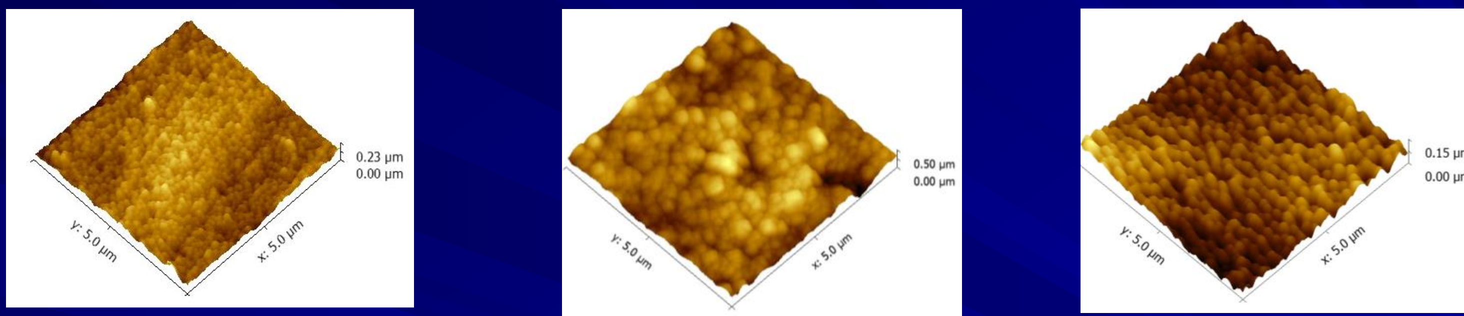


Comparative cyclic voltammograms on Al working electrode for ChCitOx and ChCitOx-IsOH-EG electrolytes at a temperature of 70°C (scan rate: 50 mV.s^{-1})

RESULTS AND DISCUSSION

Aluminum anodization

Nanoporous anodic alumina layers involving choline dihydrogen citrate based eutectic mixtures



(a) ***(b)*** ***(c)***

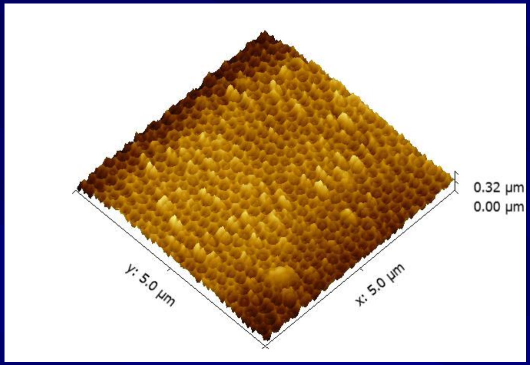
3D AFM images of anodic alumina layers after various anodization periods involving ChCitOx electrolyte (6 mA/cm^2, 60^{o}C, 80 V): (a) 1 min.; (b) 20 min.; (c) 75 min.

The beginning of the pores nucleation and formation is noticed from the first minute of anodization. Moreover, the fingerprint of the metallurgical texture of the Al substrate are still visible, due to the low thickness of the film. Further anodization results in the continuous formation of the pore structure, however showing a relative disorder of the developed porous anodic oxide arrangement. More ordered nanoporous anodic oxide film has been obtained for longer anodization periods, i.e. 75 min. in the same ChCitOx electrolyte,

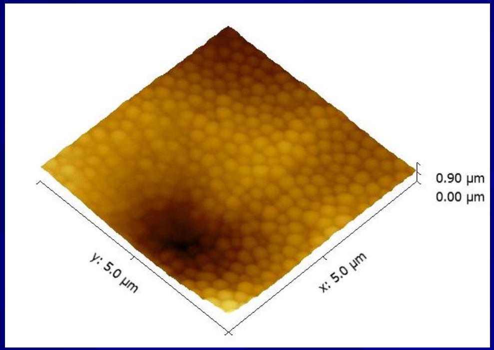
RESULTS AND DISCUSSION

Aluminum anodization

Nanoporous anodic alumina layers involving choline dihydrogen citrate based eutectic mixtures



(a)



(b)

3D AFM images of: (a) the top surface morphology of the prepared anodic alumina after the second anodization and (b) the bottom surface of the anodic alumina after Al removal (ChCitOx-IsOH-EG system, 180 min., 60°C, 80 V)

- *A quite well-ordered array of nanopores may be observed, even when a relatively high anodization temperature was applied.*
- *The pore bottom is covered by the barrier layer. The image evidences the typical closed pore bottom hemispherical caps of the porous anodic alumina, similar to those reported for other anodization electrolytes*

RESULTS AND DISCUSSION

Aluminum anodization

Nanoporous anodic alumina layers involving choline dihydrogen citrate based eutectic mixtures

Pore diameter (D_p) and interpore distance (D_{int}) of anodic alumina layers obtained from the investigated ionic liquid based electrolytes

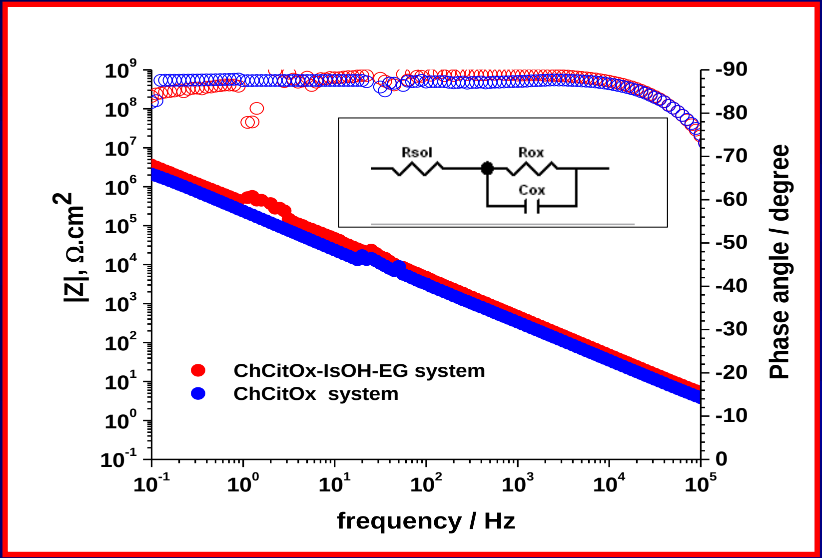
Electrolyte type/anodization voltage, V	D_p, nm	D_{int}, nm
ChCitOx/80	73-78	184-200
ChCitOx-IsOH-EG/70	52-55	157-160

RESULTS AND DISCUSSION

Aluminum anodization

Nanoporous anodic alumina layers involving choline dihydrogen citrate based eutectic mixtures

Impedance properties of the alumina anodic films



Bode plots for alumina anodic oxide layers produced in ChCitOx and ChCitOx-IsOH-EG electrolytes and recorded in 0.5 M Na_2SO_4 aqueous solution (25°C, pH 5.5, at open circuit potential). Inset: the proposed equivalent electrical circuit

Fitting results of impedance spectra of the investigated anodic oxide alumina layers using the proposed equivalent circuit

Electrolyte type	R_{sol}, Ω	R_{ox}, Ω	C_{ox}, F
ChCitOx	1.1	$4.6.10^6$	$6.8.10^{-7}$
ChCitOx-IsOH-EG	1.3	$3.1.10^7$	$3.7.10^{-7}$

The obtained data suggest that the use of ChCitOx-IsOH-EG electrolyte facilitates formation of more resistive anodic layers, showing values of the oxide resistance of one order of magnitude higher than those determined when ChCitOx electrolytes has been applied.

CONCLUSIONS

➢Ionic liquids based on eutectic mixtures of cholinium salts with different hydrogen bond donors may represent a potential environmental friendly viable alternative for aluminum electrochemical surface treatments.

➢The selection of the optimum working parameters is closely related to the Al metal characteristics (e.g. purity, composition, metallurgical treatments, heat treatment, etc.)

➢IL-NH_4NO_3 system may represent a suitable electropolishing electrolyte for Al surfaces, providing RMS roughness values comparable to those achieved involving classical acid based electrolytes.

➢It has been shown for the first time that ionic liquids based on eutectic mixtures of choline citrate are able to produce quite compact, uniform, aluminum anodic oxide layers. Homogeneous, uniform and yellowish anodic alumina layers have been obtained both in potentiostatic and galvanostatic conditions, at relatively high temperatures of 45-80^oC.

➢The highest anodization rate was of about 0.4 μm/min., at an operation temperature of 60^oC, for the ChCitOx-IsOH-EG electrolytic system.

➢Values of pore diameters between 50 – 80 nm and interpore distances in the range of 160-200 nm have been estimated from AFM and SEM investigations, influenced by the electrolyte nature and anodization conditions.

➢The recorded EIS spectra showed a pure capacitive behavior and high anodic oxide resistances of 10^6-10^7 $\Omega.cm^2$ order.

➢Future investigations are scheduled for a deeper understanding of the mechanism in the presence of different additives and a better optimization of the main parameters (e.g. temperature, current density, time, applied voltage) against the involved ionic liquid composition.

Acknowledgments.

We acknowledge funding from NANOCOATIL project , No. 7082-2013 under M ERA Net Program.

THANK YOU VERY MUCH FOR YOUR ATTENTION!