Environmentally-Friendly Cerium-Based Conversion Coatings Obtained by Cathodic Electrodeposition in Deep Eutectic Solvents Formulations for Corrosion Protection of AA7075 Aluminium Alloys

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MOTIVATION

- The detrimental impact of hexavalent chromium compounds on the environment and human health determined the European Union to restrict their use, with a significant impact on a quite large number of technological processes, including those related to Al and its alloys surface treatments.

The development of chromium-free coatings

- ***Rare earth compounds*** *are among the most promising options for replacing chromate conversion coatings on Al and Al alloys, being for the first time introduced by Hinton's group in the 1980s.* ***Cerium compounds are generally the most active ones*** *and they can be applied to Al alloys by a large range of procedures, including* ***electrolytic deposition****, spray, swabbing and immersion.*

- ***The cathodic electrochemical deposition*** *represents a potentially attractive route able to reduce the process duration and also to provide a coating developing on the whole alloy surface unlike for example, immersion coating, which can result in coatings mainly over cathodically active sites.*

- *A quite* ***novel approach*** *to form Ce-based nanostructures takes into consideration the use of the novel ionic media based on choline chloride eutectic mixtures with different hydrogen bond donor compounds, also known as "****deep eutectic solvents-DES****" or "ionic liquid analogues-ILA", as an environmentally friendly alternative for a large range of metal and alloy surface treatments.*

- *Therefore, some preliminary experimental results are presented, intending to explore* ***the use of different DES based formulations for the cathodic electrodeposition of cerium-based conversion coatings onto AA7075 aluminium alloys.***

Experimental sequence

DES based electrolytes preparation

Choline chloride: urea(1:2) (ILU)	*Choline chloride: glycerine(1:2) (ILG)*
ILU-Ce: *ILU:glycerine:ethanol (6:1:1 vol.) + 0.1 M $Ce(NO_3)_3.6H_2O$ +0.5 M H_2O_2*	**ILG-Ce**: *ILG:ethanol (1:1 vol.) + 0.1 M $Ce(NO_3)_3.6H_2O$ +0.5 M H_2O_2*

AA 7075 Chemical composition (wt. %)

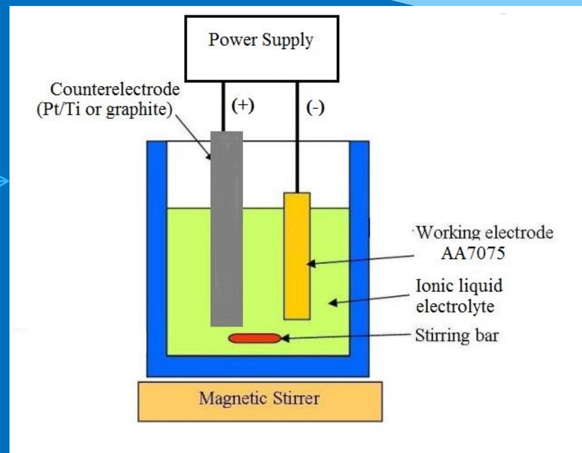
Si	Fe	Cu	Mn	Mg	Cr	Ni	Zn	Ti	Al
0.1	0.19	1.53	0.07	2.55	0.18	0.0058	5.89	0.024	Rest

Surface preparation

- *Alkaline chemical degreasing* :
  - $Na_2CO_3.10H_2O$ 30-50 g/l
  - NaOH 5 g/l t=60-80^oC for 2-5 mi
  - $Na_3PO_4.12H_2O$ 30-50 g/l
- *Chemical deoxidizing:*
  - HNO_3 1:1 (vol.), t=25-30^oC for 30-60 s
- *Rinsing*
- *Drying*

Experimental sequence

Electrochemical deposition



Post-treatment

(c) 0.1 M $Ce(NO_3)_3.6\ H_2O$
+ 0.2 M stearic acid in EtOH
t = 20 min. ;$U_{dc\ (const)}$ = 20 V; RT

Physical-chemical characterization

- *Appearance, adhesion*
- *Coating mass*
- *SEM-EDX*

Accelerated corrosion tests:

(i) continuous immersion in 0.5M NaCl at 25 °C for 720 hours with intermediary visual examinations and recording of corrosion potential;

(ii) potentiodynamic polarization curves (1 mV/s, against Ag/AgCl reference electrode and a Pt counterelectrode; WE – the investigated coating with a geometrical constant surface of 0.19 cm^2)

(iii) impedance spectra at open circuit potential, in 0.5M NaCl;

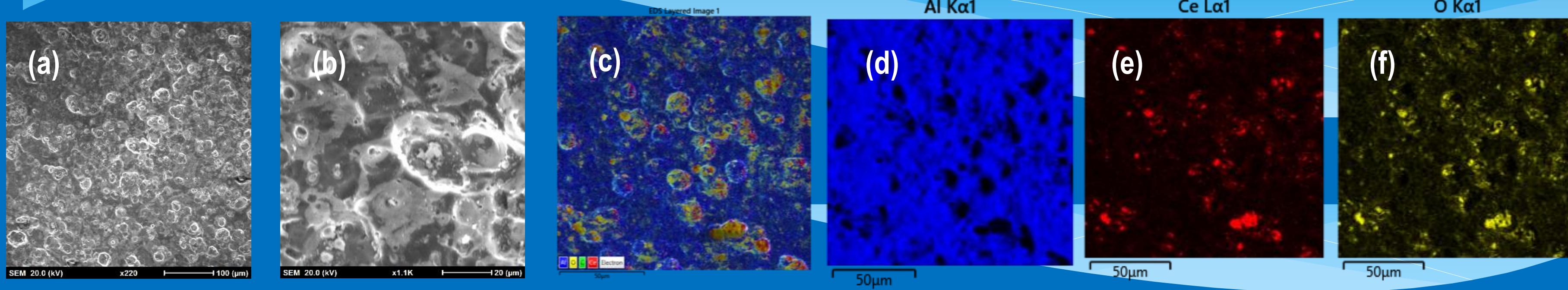
- *All electrochemical tests have been performed using a PARSTAT 4000 potentiostat controlled with VersaStudio software; min. 3 pcs. for each variant, specimens of 70x35 mm*

(iv) Salt mist test (in accordance with CEI 68-2-11, Ka method)*;*

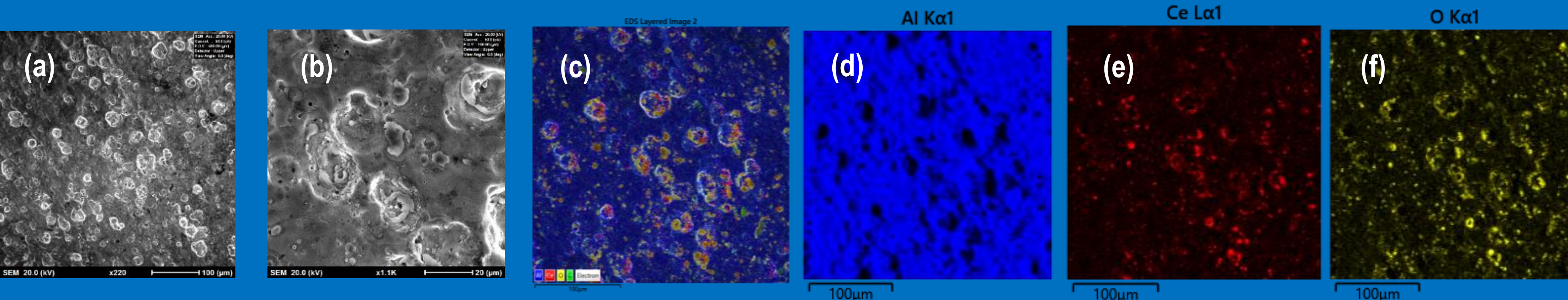
- *min.3 pcs. for each variant, specimens of 70x35 mm;*
- *intermediary examinations after 24, 48, 72, 144, 168, 192, 240 hours;*

RESULTS AND DISCUSSION

Ce-based electrodeposited conversion coatings involving ILU - Ce system



SEM micrographs at different magnifications (a, b) and EDX maps (c, d, e, f) showing the distribution profiles of the significant elements within the Ce based deposit (ILU-Ce, 10 mA cm^{-2}, 15 min., RT)



SEM micrographs at different magnifications (a, b) and EDX maps (c, d, e, f) showing the distribution profiles of the significant elements within the Ce based deposit (ILU-Ce, 20 mA cm^{-2}, 10 min., RT)

Quite irregular rounded particles of about 10-15 µm, covering almost entirely the Al alloy substrate

Based on EDX measurements, the Ce based deposits contained 0.31 – 4.8 wt.% Ce, depending on the operation conditions. Higher Ce content was noticed for higher current density values and for longer process durations, too. The presence of C has been also observed, suggesting a potential incorporation of the electrolyte in the coating.

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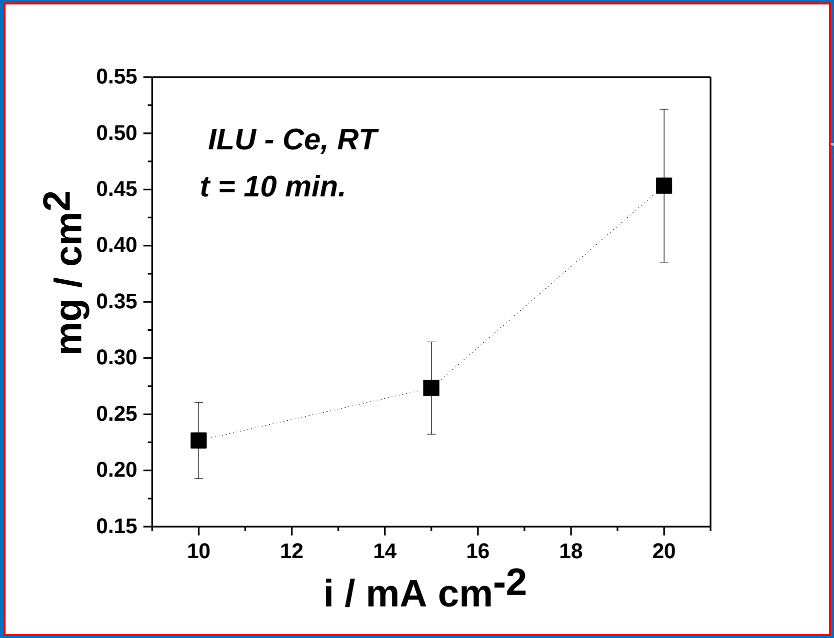
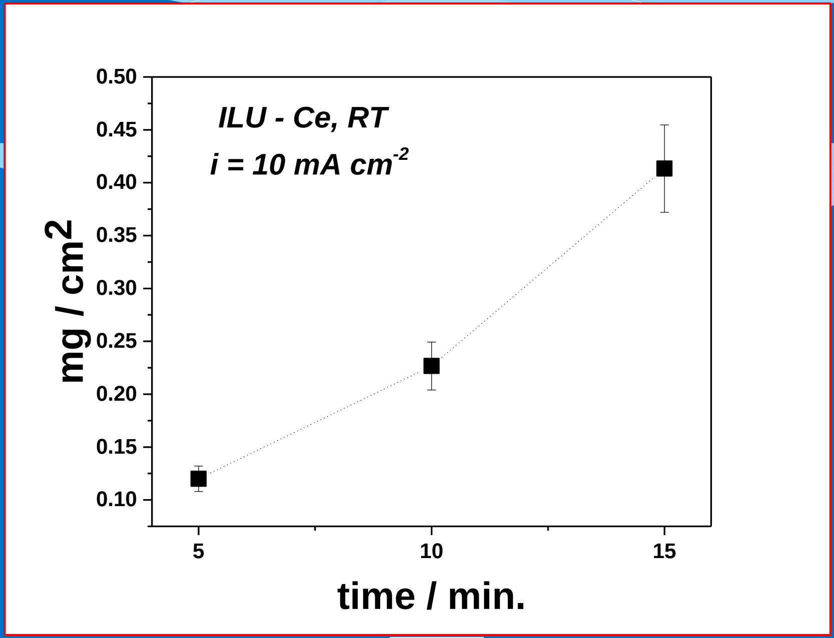


(A)

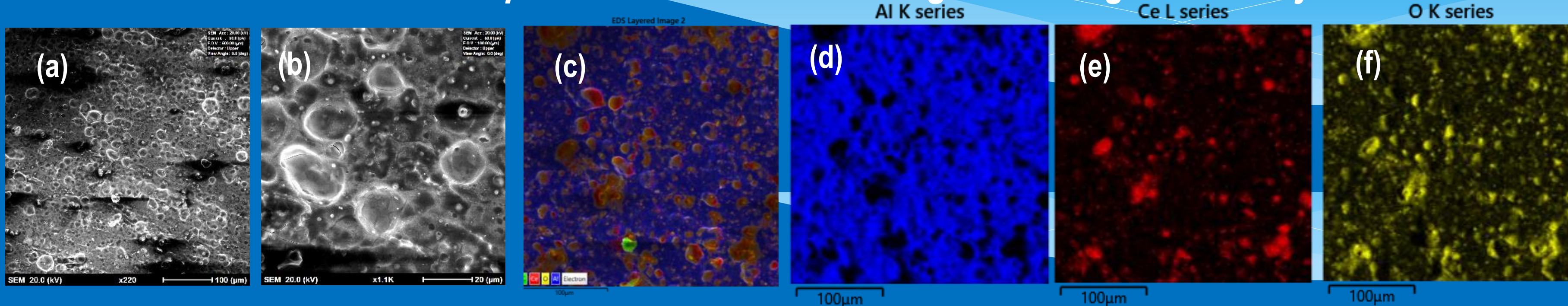


(B)

The influence of : (A) current density and (B) electrochemical process duration on the coating mass of the Ce-based coating using ILU-Ce system

RESULTS AND DISCUSSION

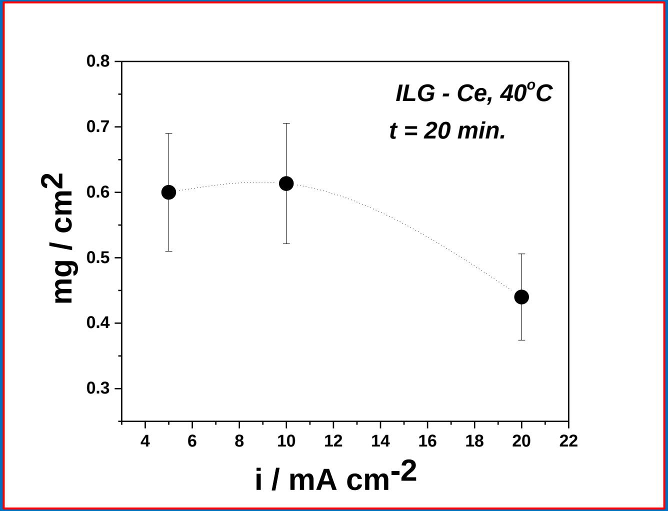
Ce-based electrodeposited conversion coatings involving ILG - Ce system

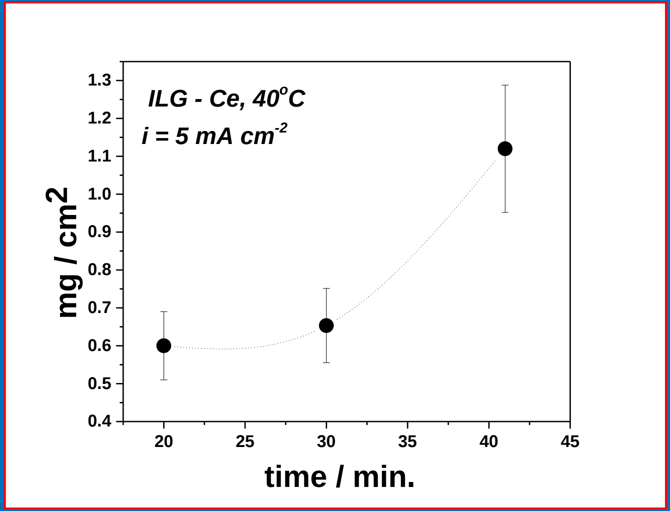


SEM micrographs at different magnifications (a, b) and EDX maps (c, d, e, f) showing the distribution profiles of the significant elements within the Ce based deposit (ILG-Ce, 5 mA cm^{-2}, 30 min., 40 ^{o}C)

Ce content: 0.43 – 1.56 wt.% (EDX analysis)

(A)



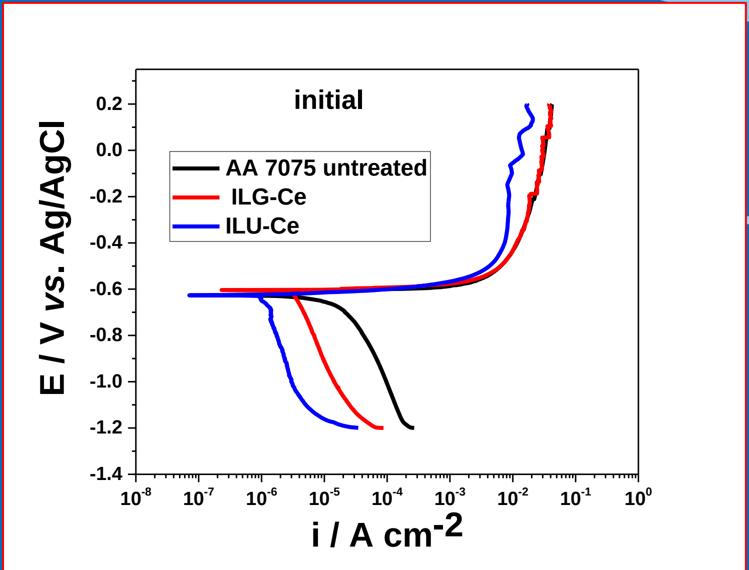


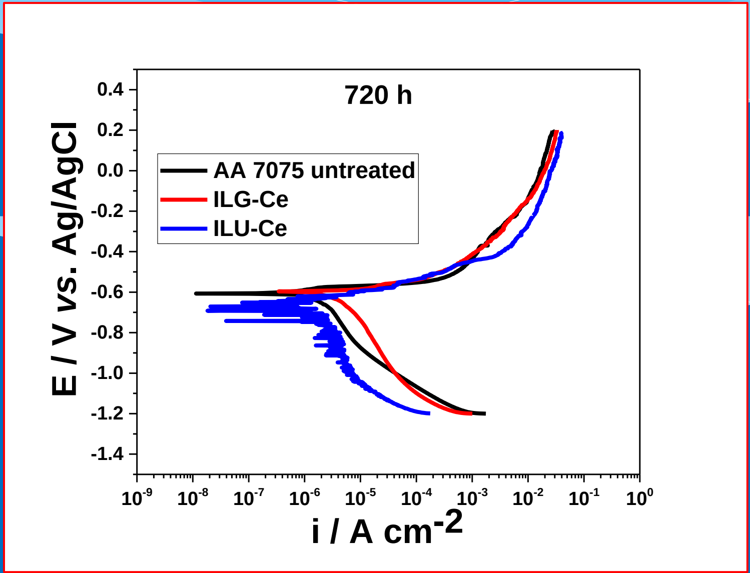
(B)

The influence of : (A) current density and (B) electrochemical process duration on the coating mass of the Ce-based coating using ILG-Ce system

RESULTS AND DISCUSSION

Corrosion behaviour of Ce- based conversion coatings on AA 7075 obtained from DES based systems





Polarization curves in semilogarithmic coordinates for Ce- based conversion coatings on AA 7075 obtained from DES systems during continuous immersion test in 0.5M NaCl (initial and after 720 h of conditioning, 25°C, 1 mV.s^{-1})

Characteristic values resulted from polarization curves experiments in 0.5M NaCl

Coating system	Initial		After continuous immersion for 720 h	
	E_{cor}, V vs.Ag/AgCl	I_{cor}, $\mu A/cm^2$	E_{cor}, Vvs.Ag/AgCl	I_{cor}, $\mu A/cm^2$
AA 7075 untreated	-0.713	32.1	-0.601	19.6
ILG - Ce	-0.717	5.61	-0.720	7.61
ILU - Ce	-0.690	1.43	-0.660	0.77

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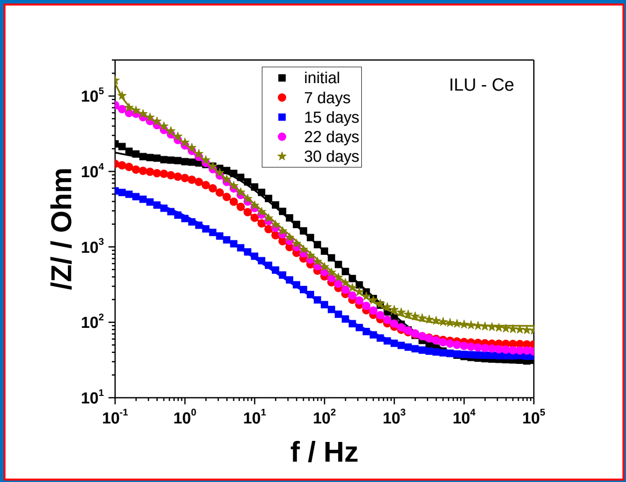
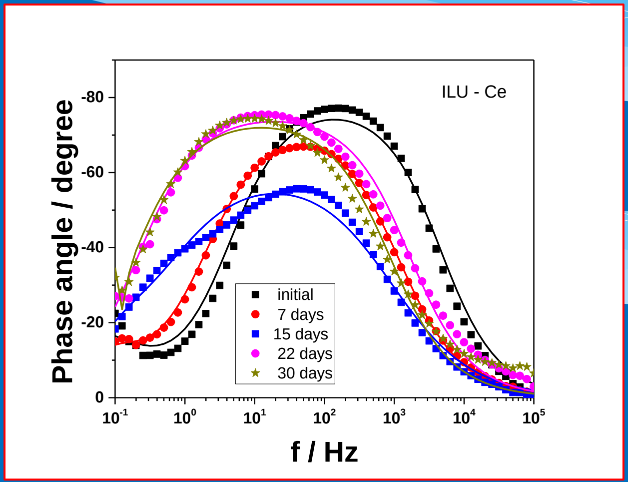
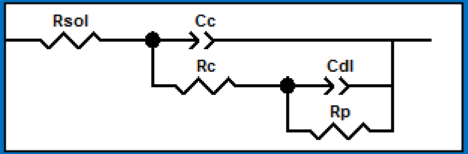
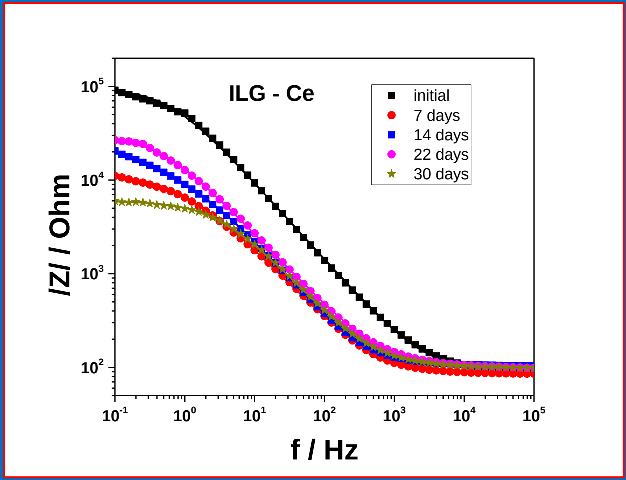
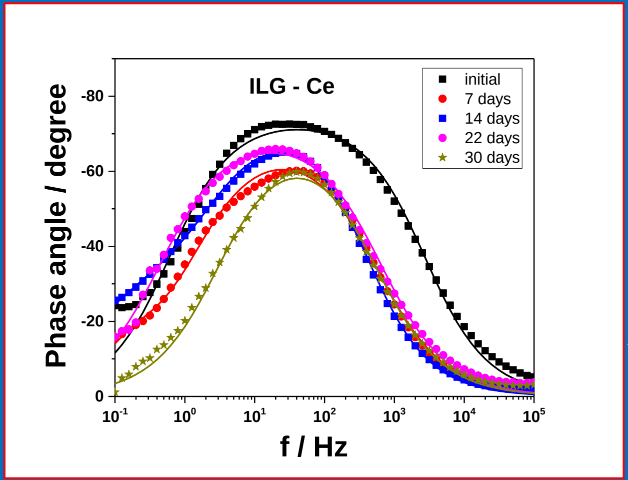






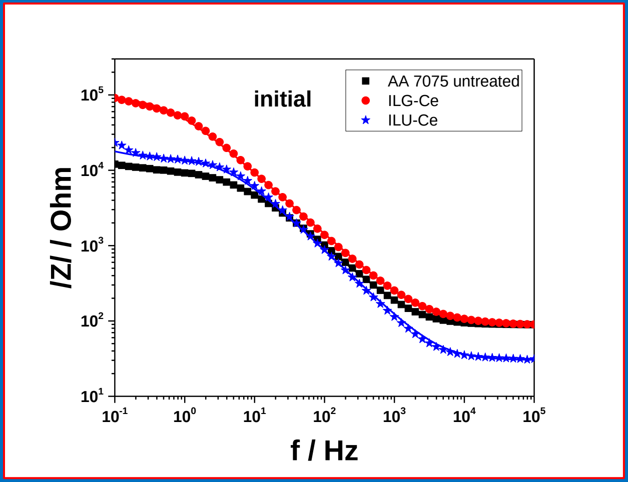


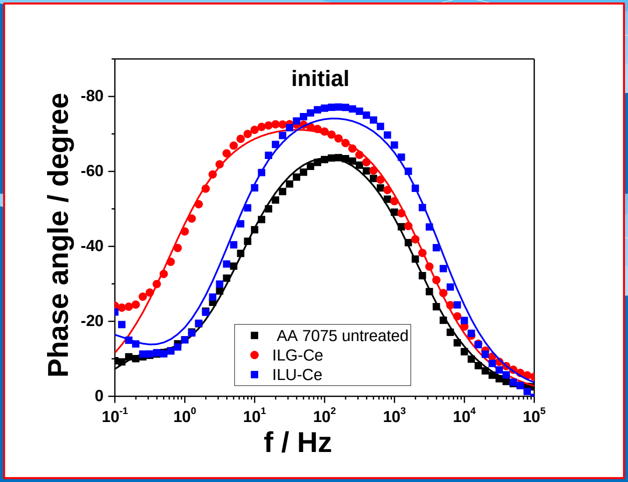


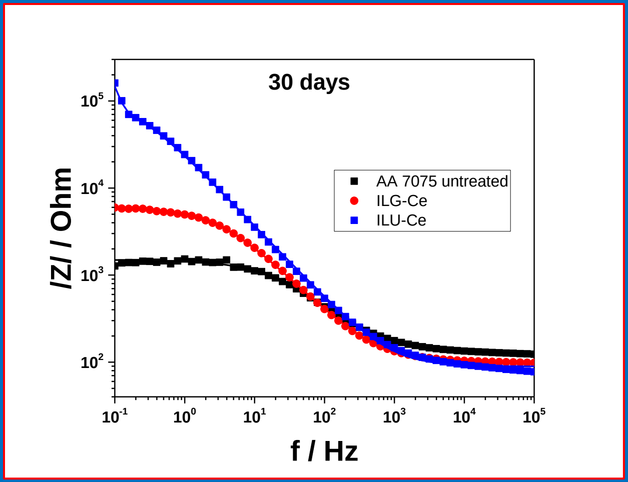
Comparative Bode plots in 0.5M NaCl at open circuit potential, after various continuous immersion periods for Ce- based conversion coatings involving ILU –Ce and ILG-Ce systems (solid lines are the fit to the measured points using the proposed equivalent circuit)

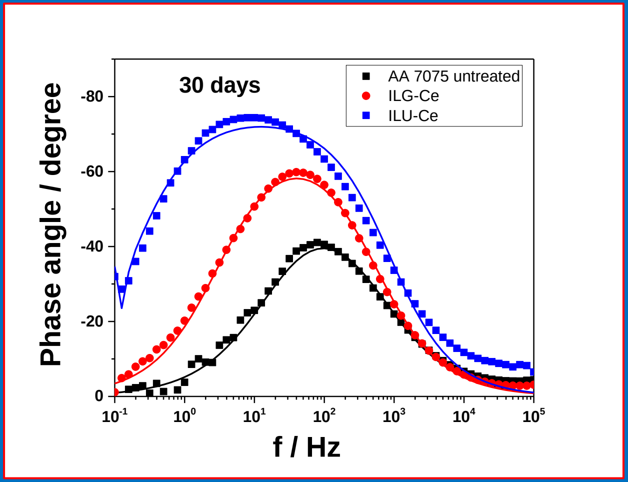
RESULTS AND DISCUSSION

Corrosion behaviour of Ce- based conversion coatings on AA 7075 obtained from DES based systems





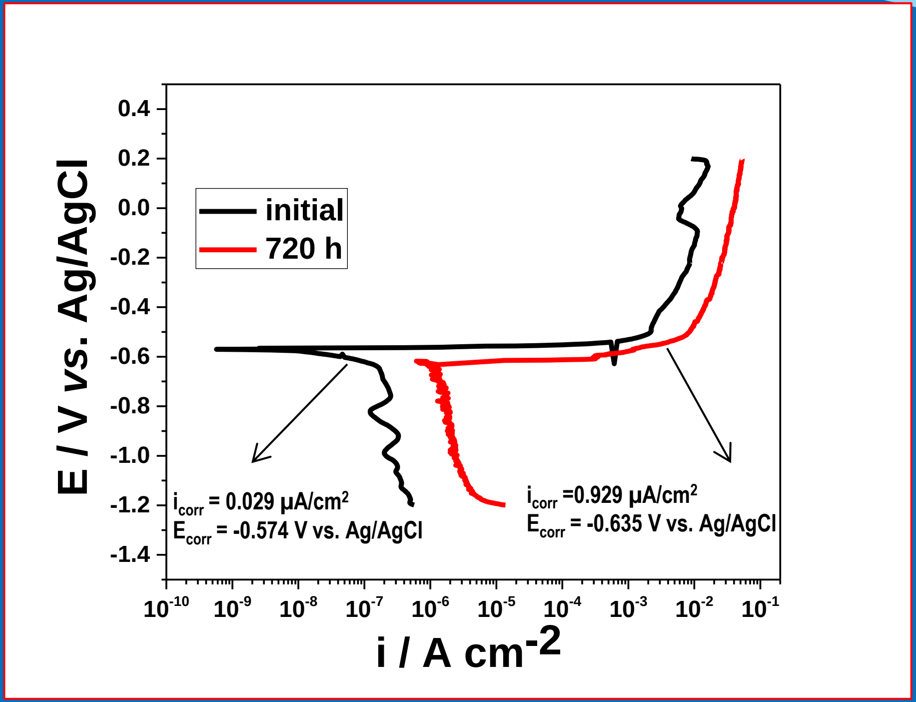




Comparative Bode plots in 0.5M NaCl at open circuit potential, for Ce- based conversion coatings involving ILU –Ce and ILG-Ce systems and untreated AA 7075 for the initial and final conditioning period (solid lines are the fit to the measured points using the proposed equivalent circuit)

RESULTS AND DISCUSSION

Corrosion behaviour of Ce- based conversion coatings on AA 7075 obtained from DES based systems. The influence of the post-treatment



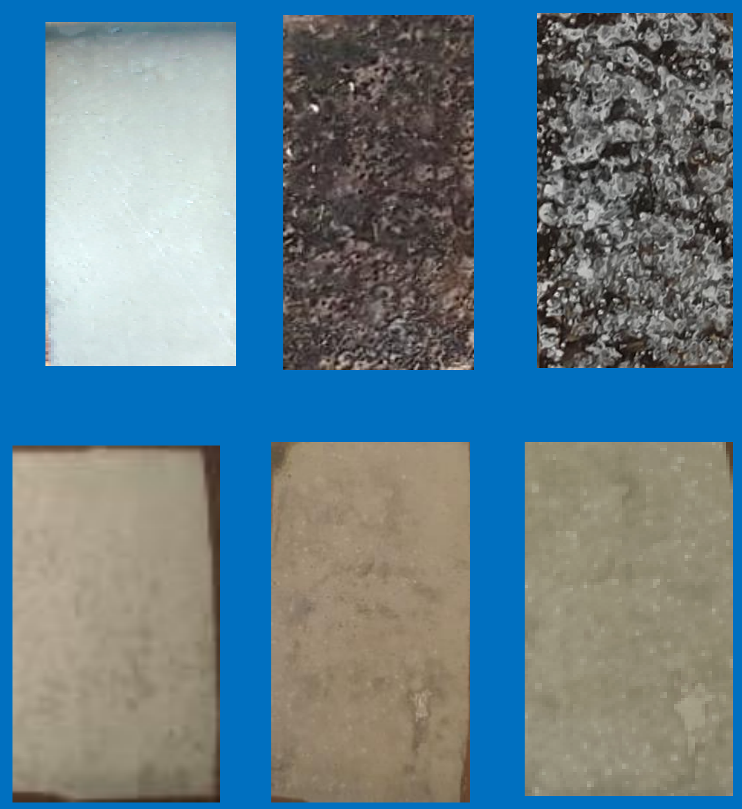
Polarization curves in semilogarithmic coordinates for Ce- based conversion coating on AA 7075 obtained from ILU-Ce system subjected to post-treatment during continuous immersion test in 0.5M NaCl (initial and after 720 h of conditioning, 25°C, 1 mV.s^{-1})

RESULTS AND DISCUSSION

Corrosion behaviour of Ce- based conversion coatings on AA 7075 obtained from DES based systems. The influence of the post-treatment

Salt mist test

initial | *96 h* | *240 h*



AA 7075 untreated

Ce- based conversion coating on AA 7075 obtained from ILU-Ce system subjected to post-treatment

CONCLUSIONS

- *The electrochemical deposition of cerium based conversion coatings involving different DES based formulations onto AA7075 aluminium alloys has been explored.*

- *Electrolytes containing $Ce(NO_3)_3.6H_2O$ dissolved in choline chloride-glycerine (1:2 molar ratio) and choline chloride-urea (1:2 molar ratio) , with additions of H_2O_2 and other components to provide a proper adhesion and growth rate have been proposed.*

- *The EDX investigations confirmed the presence of Ce within the deposited coatings in the range of 0.3 – 5 wt. %. The electrolytes based on choline chloride-urea eutectic mixture appeared to facilitate a higher Ce content (up to ~ 4.8 %) depending on the applied operation conditions.*

- *The corrosion performance of the coatings was assessed through polarization measurements and EIS for long immersion periods of 720 h. The Ce-based coatings electrochemically prepared in choline chloride-urea eutectic mixture showed the best corrosion protection , i.e. the lowest corrosion current and the highest R_p values even after 720 h of conditioning in 0.5 M NaCl.*

- *The use of an additional post-treatment step might improve the corrosion characteristics.*

- *Further investigations will be performed, for a better understanding of layer formation mechanism associated with the obtained morphology as an important factor to influence corrosion protection mechanisms.*

Acknowledgements

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THANK YOU VERY MUCH FOR YOUR ATTENTION!