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Abstract: Aluminium electrodeposition from ionic liquids (ILs) prepared using a novel structure composed by perfluoro-3-oxa-4,5 dichloro-pentan-sulphonate [CF2ClCFClOCF2SO3-] and different cations is presented. The novel anion was designed by Solvay Specialty Polymers with the purpose to confer to the ionic liquids strong hydrophobic properties that facilitate the aluminium deposition in ambient conditions. Three cations, imidazolium, pyridinium and guanidinium are used to prepare the corresponding three liquids. In water, the resulting liquids prepared with imidazolium and pyridinium show very low miscibility and the liquid prepared with guanidinium is insoluble. Their electrochemical windows are dependent of both the cations and the substrate nature and are sufficiently wide to allow aluminium deposition. Even so, it was evidenced that the reduction of the new structure is not especially difficult. The AlCl3 was selected as useful source of Al(III) electroactive species to obtain coherent deposits. Using aluminium hydroxide, the coalescence of the aluminium deposits was not achieved. The viability of aluminium electrodeposition was, at first, tested on vitreous carbon, demonstrating it follows through a nucleation and growth process. As the practical interest carries to the use of metallic substrata, nickel was selected to analyse deposition process. The deposits prepared at constant current showed a better appearance, less stressed and smoother than the ones prepared at constant potential. The effect of temperature and concentration was studied in solutions prepared with tetramethyl guanidinium-perfluoro-3-oxa-4,5 dichloro-pentan-sulphonate, taking advantage of its immiscibility in water. Deposits prepared from the lower concentrations tested (AlCl3:IL 0.95:1 molar ratio) were continuous, fine grained and stress-free, provided that they were obtained at moderate applied current. From higher Al(III) concentration solutions it was only possible to allow stress-free deposits by applying low currents.

Barcelona, 26 April 2018

Dear Editor

Please find enclosed the revised version of the manuscript entitled "**Electrodeposition of Aluminium from hydrophobic perfluoro-3-oxa-4,5 dichloro-pentan-sulphonate based ionic liquids**" in which the English language has been checked and references adjusted to format.

The authors believe that it will be considered suitable for publication in *Journal of Electroanalytical Chemistry.*

Yours sincerely,

Elvira Gómez

Highlights

- Aluminium electrodeposition from a new hydrophobic solvents.
- Hydrophobic anion and work temperature allow deposition process in ambient conditions.
- Preparation under constant applied current favours stress-free deposits versus potentiostatic deposition.
- Stress is minimized by tailoring applied current, $AlCl_3$ content and temperature.

REVIEWER 1

We would like to thank the Reviewer for the favourable comments and for the suggestions to improve the quality of the manuscript.

The text has been revised trying to avoid repetitions in the information and improving the structure of the sentences throughout the manuscript. The experimental section has been written more concisely.

No changes have been made to the figures

Electrodeposition of Aluminium from hydrophobic perfluoro-3-oxa-4,5 dichloro-pentan-sulphonate based ionic liquids

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Abstract

Aluminium electrodeposition from ionic ==liquids (ILs) prepared== using a novel structure composed by perfluoro-3-oxa-4,5 dichloro-pentan-sulphonate [$CF_2ClCFClOCF_2SO_3^-$] and different cations is presented. The novel anion was designed by Solvay Specialty Polymers with the purpose to confer to the ionic liquids strong hydrophobic properties that facilitate the aluminium deposition in ambient conditions. Three cations, imidazolium, pyridinium and guanidinium are used to prepare the corresponding three liquids. In water, the resulting liquids prepared with imidazolium and pyridinium show very low miscibility and the liquid prepared with guanidinium is insoluble. Their electrochemical windows are dependent of both the cations and the substrate nature and are sufficiently wide to allow aluminium deposition. Even so, it was evidenced that the reduction of the new structure is not especially difficult. The $AlCl_3$ was selected as useful source of Al(III) electroactive species to obtain coherent deposits. Using aluminium hydroxide, the coalescence of the aluminium deposits was not achieved.

The viability of aluminium electrodeposition was, at first, tested on vitreous carbon, demonstrating it follows through a nucleation and growth process. As the practical interest carries to the use of metallic substrata, nickel was selected to analyse deposition process. The deposits prepared at constant current showed a better appearance, less stressed and smoother than the ones prepared at constant potential. The effect of temperature and concentration was studied in solutions prepared with tetramethyl guanidinium-perfluoro-3-oxa-4,5 dichloro-pentan-sulphonate, taking advantage of its immiscibility in water. Deposits prepared from the lower concentrations tested ($AlCl_3$:IL 0.95:1 molar ratio) were continuous, fine grained and stress-free, provided that they were obtained at moderate applied current. From higher Al(III) concentration solutions it was only possible to allow stress-free deposits by applying low currents.

Keywords: aluminium electrodeposition, hydrophobic ionic liquid, vitreous carbon substrate, nickel substrate, open-air system

1. Introduction

Lately the plating of aluminium (Al) has been widely investigated due to its potential applications (both aesthetic and functional) including corrosion protection [1, 2], decorative coatings [3], electrorefining processes [4, 5], electronics [6], and current collectors in Al-ion

batteries [7-9]. Applications that have an important industrial role due to the low cost, low density and environmentally benign nature of aluminium.

Much research has been done on several methods for the preparation of aluminium deposits. Among those currently available are electrodeposition, thermal processing (thermal spray coating and hot dipping) [10-13], or low pressure vapour phase deposition, PVD [14] and CVD [15]. However, some of these methods are quite expensive, technically demanding and do not permit obtaining thin films.

In fact, electrodeposition is the preferred method as it is simple, cost-efficient, has low energy consumption, can be used on objects with complex shapes and implies relatively easy control. Unfortunately, given the low standard potential of Al(III)/Al couple, the use of aqueous baths for aluminium deposition is unsuitable. Therefore, aluminium electrodeposition has been carried out using either organic solvents [16-19] or inorganic molten salts [20], but both kinds of solutions present strong limitations related to their flammability and corrosive action. Such drawbacks have led to study the possibility of using Ionic Liquids (ILs) as electrochemical media for aluminium electrodeposition since they do show some promising results.

In the past two decades, numerous groups have studied the electrodeposition of aluminium using ionic liquids. ILs show attractive physicochemical properties, including a wide electrochemical window (that can be tailored by modifying the ionic components), low vapour pressure, high intrinsic conductivities, moderate viscosities and high boiling point that make them also, environmentally friendly. Most of the work related to aluminium electrodeposition in ionic liquids has been done using chloroaluminate ILs (the so-called first generation ILs), in which the $[Al_2Cl_7]^-$ complex formed in the Lewis acidic melt can be reduced to metallic aluminium [21, 22]. Plating solutions are easy to prepare by simple addition of the Lewis acid $AlCl_3$ to N,N´-dialkyl-imidazolium chloride [23-32], alkyl-pyridinium chloride [33], N-alkylpyrrolidinium [34, 35] or to quaternary ammonium compounds [36, 37] under an inert atmosphere. Such media are, however, moisture sensitive and the solutions require strictly controlled conditions. A second class of liquids was subsequently developed (known as air-and water stable ILs) which presented an improved hydrophobicity due to their particular anionic structures. Some of them are tetrafluoroborate (BF_4^-), trifluoromethylsulfonate ($CF_3SO_3^-$), bis(trifluoromethylsulfonyl)-imide $[(CF_3SO_2)_2N^-]$, and tris(trifluoromethylsulfonyl)methide $[(CF_3SO_2)_3C^-]$. While aluminium was deposited using these liquids [38-41], it was found that long exposures to temperature and atmospheric humidity could change their physicochemical properties [42]. For these reasons, these solutions needed to be used under inert atmosphere in order to prevent degradation.

From the aforementioned problems, it can be easily understood that the industrial processing of aluminium electrodeposition has still not been well mastered, and the finding of a moisture-resistant route to aluminium electrodeposition remains still to be found.

Recently different proposals have been put forward in order to solve the technological problems of aluminium deposition. Thus, researchers proposed the possibility of electrodepositing functional aluminium layers from an $AlCl_3$/ionic liquid in ambient conditions, by insulating the electrolyte from air with a layer of a specific hydrocarbon compound [43, 44] and this did indeed enable aluminium to be deposited outside the glove box. Other alternatives proposed involve the use of $AlCl_3$-based ionic liquids with a neutral substituted ligand. Such liquids have been prepared using group V nitrogen-based ligands. Recently, since group VI elements possess also single electron pair, Al-ILs based on ligands with O and S have been introduced and investigated. These new ILs based on complexation with neutral ligands are formed by interaction between the ligands and $AlCl_3$, to produce Al-containing ions by the asymmetric cleavage of $AlCl_3$.

The liquids prepared differ fundamentally from first generation ones, since the positive charge is placed on the aluminium, whereas in the previous ones the electroactive species were negative. This can be beneficial as the electroactive cationic metal complexes can easily reach electrode surface. Abbott et al. [45] reported that simple neutral amides (acetamide and urea) could be mixed with $AlCl_3$ to form room-temperature ILs, which have been used for aluminium electrodeposition. These ILs however, cannot shield effectively the aluminium centre and, consequently, are still moisture sensitive. Alternatively, new proposals involving complexing agents containing aromatic rings are being analysed with the idea that the ring's presence could mitigate moisture sensitivity [46-49]. The development of such ILs using readily available and relatively hydrophobic "neutral" ligands could be of great interest for the practical electroplating of aluminium.

It is known that both chain length and nature of the anion in the ionic liquid have an influence on electrochemical behaviour. Considering this united to the fact that the hydrophobicity of the IL is specific of the anionic structure, the present work is focused on systems in which the anion hydrophobicity has been enhanced as a possible way to overcome the Achilles' heel of aluminium electrodeposition in open systems. For this, the use of new perfluoroalkyl sulfonate salts has been developed and studied in collaboration with the R&D centre of Solvay Specialty Polymers, which possess high expertise in fluorinated products and organic synthesis. In this work we present results obtained with three ionic liquids prepared combining an innovative anion, perfluoro-3-oxa-4,5 dichloro-pentan sulphonate $[CF_2ClCFClOCF_2CF_2SO_3]$, with three

different conventional cations: N,N-dimethyl imidazolium (IMI as acronym of the liquid), tetramethyl guanidinium (GUA as acronym of the liquid) and 1,2,4,6-tetramethyl pyridinium (PYR as acronym of the liquid). These products lead to water- and air stable ionic liquids even after adding the aluminium source, being interesting systems for the study of aluminium plating in an open system.

In a previous work, an exhaustive study was performed on vitreous carbon substrate using GUA as solvent [50], in which aluminium electrodeposition was demonstrated in a wide range of $AlCl_3$:IL molar ratios. This work focuses on the study of aluminium deposition process from liquids in which the hydrophobic character was enhanced, extending the analysis to metallic substrates, because the final technological interest is the deposition on polymeric substrates functionalized with metallic seed layer. Aluminium electroplating from $AlCl_3$ on vitreous carbon was checked from solutions prepared with PYR and IMI. The possibility to deposit from aluminium hydroxide as a source of electroactive Al(III) species was also explored. Deposition on metallic substrates was carried out under different potentiostatic and/or galvanostatic conditions. The prepared deposits were characterized using scanning electron microscopy. The influence of some electrodeposition conditions like Al(III) concentration and temperature was analysed.

2. Experimental

The behaviour of three novel ILs sharing the same anion perfluoro-3-oxa-4,5-dichloro-pentan-sulphonate $[CF_2ClCFClOCF_2CF_2SO_3^-]$, N,N-dimethyl imidazolium (IMI), tetramethyl guanidinium (GUA) and 1,2,4,6-tetramethyl pyridinium (PYR) supplied by Solvay Specialty Polymers, was studied. Blank solutions were prepared by melting a weighted amount of IL using a silicone bath under inert atmosphere and stirring conditions. The melting points of the liquids are for IMI 56ºC, for GUA 71ºC and for PYR 78ºC. In water, GUA is insoluble and IMI and PYR show very low solubility.

Conductivity was measured at different temperatures using a Metrohm 644 conductometer with a 52-92 Crison^{TM} conductivity cell (1 cm^{-1} of cell constant). The cell contained two parallel platinum sheets, the temperature was controlled with an accuracy of 0.3ºC using a Pt (100 ohm) resistor from Kosmon.

The electroactive solutions were prepared by dissolving the pertinent aluminium reactant, in the IL following the protocol: The weighed amount of IL was melted in nitrogen atmosphere in a Schlenk flask. Once liquefied the IL, the weighed amount of $Al(OH)_3$ (from Cymit) or $AlCl_3$ (from Sigma-Aldrich) was added to obtain the desired Al(III):IL molar ratio. $Al(OH)_3$ and

AlCl$_3$ dissolve well and homogeneously although slowly in the ILs under stirring and heating at 100ºC. The appearance of the solutions was different in each case, being caramel-like in AlCl$_3$-GUA, white and thick in AlCl$_3$-IMI and yellowish in AlCl$_3$-PYR, whereas all solutions obtained from Al(OH)$_3$ were white. Using PYR was necessary moderate agitation, otherwise a gum ball was formed. Solutions with concentration lower than 0.9:1 Al(III):IL were not considered according to the previous results obtained [50].

The electrochemical study was carried out using an Autolab with PGSTAT30 equipment and GPES software. A thermostatically-controlled three electrode open cell of a single compartment was used. Working electrodes were glassy carbon rod of 2 mm of diameter from Metrohm or small sheets (effective area 0.25 cm^2) of nickel or copper from John Matthey. The glassy carbon was polished to mirror finish using alumina of different grades (3.75 and 1.87 µm), cleaned ultrasonically for 2 min in water and dried with air prior to be immersed in the solution. Using nickel or copper as working electrodes, they were dipped in a solution of nitric acid (1:1) and afterwards polished with alumina 1.87 µm. Aluminium and platinum wires were used as pseudo-reference and counter electrodes respectively. Aluminium wire was mechanically polished with Struers SiC 4000 paper and platinum wire was heated in a flame to incandescence during several minutes after immersion in a nitric acid solution (1:1). Water remained was removed with nitrogen flow prior to the immersion of electrodes in the solution.

Voltammetric experiments were performed at scan rate of 10 mVs^{-1}, in favour of recording accurate curves. The experiments were done scanning first to negative potentials. Chronoamperometric experiments were performed starting from a potential were no process took place and jumping to the selected potential value. Galvanostatic curves were recorded at different currents selected according previous voltammetric results. Deposits were prepared by means of potentiostatic and galvanostatic techniques and after were quickly removed from the solution and carefully washed, first in warm dichloromethane, then in a dichloromethane-acetone mixture and finally in acetone.

Experiments were made using fresh substrates and the working temperature was 100ºC unless otherwise stated.

A scanning electron microscope Field Emission JSM-7100F Analytical Microscopy was used to study the morphology of the films. Energy dispersive X-ray analysis allowed to determine the elemental composition of the deposits.

3. Results and discussion

3.1. Ionic liquids characterization

The conductivity of the ILs was measured, from their melting temperature up 120ºC in order to get information about adequate work temperature range. As observed previously for GUA [50], an increase of the temperature leads to a rise in the conductivity (Fig.1), being the values for IMI and PYR slightly higher than those measured for GUA.

Due to the intrinsic high melting temperature of the ILs, the electrochemical experiments were performed at 100ºC, in order to assure reasonable conductivity for the future deposition purpose. The voltammetric window was established using three different working electrodes, vitreous carbon, nickel and copper, starting at potential values at which current did not appear and scanning towards negative potential values. Figure 2 shows the recorded voltammetric profiles on nickel substrate.

The comparison between the three substrates (Fig. S1) shows that the appearance of the massive reduction current is directly linked to the nature of the substrates. Reversing the scan some reduction current was maintained along the positive scan. Copper is the substrate with the narrowest electrochemical window, starting the oxidation at around 0V, related to substrate oxidation. The electrochemical windows are dependent on the temperature, lowering the working temperature the effective window was widened, as was observed for GUA liquid [50].

As an alternative characterization test of these synthetized ionic liquids, the interest was centred on the evolution of the potential value under different current demand, as a tool to ascertain the feasibility of oxidation (reduction) of these liquids on the selected substrates. Currents were lead to both positive and negative values with the purpose of evaluating the easiness of the reduction (oxidation) processes.

Figures 3 and S2 show the chronopotentiometric responses corresponding to the demand on quiescent conditions of six different current densities, three negative and three positive for GUA and PYR on nickel substrate. In order to achieve the demanded current, the potential value evolves to a more negative (positive) potential, depending on both the sign and the current value. Increasing the time the potential tends to quasi-stationary value, more negative (positive) as the negative (positive) demanded current has higher absolute value. On these liquids, the general trend shows that, the differences between the corresponding stationary potential values achieved for the positive demanded currents were greater than for the negative

ones. Greater easiness was observed for the reduction process than for the corresponding oxidation. The selected counter cations seem less electroactive than the synthetized anion. Similar general behaviour was observed from GUA on vitreous carbon [50].

3.2. Aluminium deposition from Al(OH)₃

Due to the novelty of the anion two possible sources for Al(III) electroactive species were analysed, aluminium hydroxide (Al(OH)$_3$) and aluminium chloride (AlCl$_3$).

The feasibility of deposition using aluminium hydroxide was demonstrated by electrochemical results and imaging analysis. The voltammetric curves recorded on vitreous carbon show a small band before a sudden increase in the reduction current (Fig. 4A). The Al-deposition was proposed after the recording of the typical current nucleation loop observed when reversing the scan in the potential zone related to the sudden current increase (inset Fig. 4A) [51]. However, current loop was not recorded reversing the scan in the potential zone of the first band.

Although the aluminium reduction occurs, the imaged deposits obtained potentiostaticaly at different conditions trough j-t transients similar to those in Fig. 4B, show that the deposits were non-coherent and lack of compactness. At low overpotentials are porous and seem spongy (Fig. 4C, S3A), while the obtained at high overpotentials are constituted by blocks or sheets distributed randomly along the substrate (Fig. 4D, S3B). Modifying the electrodeposition conditions it was not possible to get enough improvement in the quality of deposits from this aluminium source.

Attending these preliminary results, the use of aluminium hydroxide was abandoned and the efforts were focused on the deposition process using AlCl$_3$ as electroactive species source.

3.3. Aluminium deposition from AlCl₃

After soaking the copper substrate in the prepared AlCl$_3$:IL solutions from the three liquids, chemical attack on copper surface was observed, reason that forced to discard its use as substrate. This chemical attack was especially evident when the tested substrate was a very thin copper layer deposited over flexible polymer (Fig. S4).

3.3.1 Electrodeposition on vitreous carbon

At first the objective was to trace the feasibility of aluminium deposition on vitreous carbon from AlCl$_3$ solutions (AlCl$_3$:IL 1.1:1 molar ratio) prepared using IMI and PYR ionic liquids, as previously demonstrated using GUA as solvent [50]. For both solutions the voltammetric features were similar. Figure 5A shows the voltammograms recorded at different negative limits, in which can be observed that, a current band (C$_1$) appears previous to sudden current

increase. In the inset of the figure 5A, it can be appreciated that reversing the scan in the C_1 potential range, a nucleation current loop does not appear. The process involved in the C_1 band is not related to new phase formation. Elonging the scan a peak/shoulder C_2 was developed. Figure 5B shows two consecutive voltammograms, in which the appearance of the nucleation loop after reversing the scan in the potential zone of C_2 peak (Fig. 5B curve a) evidences that a new phase is formed by nucleation and growth mechanisms at more negative potentials than those of C_1 band. The advancement of the onset of the current appearance in the second scan (Fig. 5B curve b) evidences that the process takes place on favoured conditions, on freshly deposited aluminium. Altogether it indicates that the bulk deposition of aluminium from these solutions occurs.

Aluminium deposits were prepared at constant potential under a regime in which monotonic current increase was observed in the recorded j-t transients, confirming newly the feasibility of aluminium deposition from these $AlCl_3$:IL solutions (Fig. 6A). The deposits prepared at low overpotentials show nodular morphology (Fig. 6B) with rounded grains similar to the previous one obtained from GUA [50]. Imaging the deposits prepared at more negative potentials, a grain reduction was observed (Fig. 6C), but increasing the overpotential, very stressed deposits were obtained, for which the grain was hardly recognizable (Fig. 6D). Increasing the $AlCl_3$:IMI molar ratio, similar behaviour was observed. Nevertheless, the preparation of solutions of higher $AlCl_3$ concentrations using pyridinium (PYR) was not feasible, because rubber-like ball-aggregates were formed.

3.3.2 Electrodeposition on nickel

Due to the problems involved in the preparation of the solutions using PYR, onwards the aluminum deposition study on nickel was restricted to IMI and GUA solvents.

Voltammetric experiments conducted on nickel substrate exhibit quite a similar behaviour for both kind of solutions. The voltammetric C_1 band observed on vitreous was not detected, and elonging the scan the sudden current increase related to bulk deposition moderates and shows the appearance of an incipient reduction peak (Fig. 7A). Figure 7B shows the cyclic voltammograms recorded from three different $AlCl_3$:GUA molar ratios, the reduction current appears at less negative potentials increasing the $AlCl_3$:IL molar ratio. The typical nucleation loop appears after reversing the scan at moderate overpotentials (Fig. 7B curves a and b). The presence of a clear reduction peak related with a certain mass control is evident for the lower $AlCl_3$:IL molar ratio investigated (Fig.7B curve c). Figure 7C shows the voltammograms obtained at similar conditions from solutions prepared from the two solvents, evidencing that

the aluminium deposition process is slightly more favourable in the solution prepared using guanidinium. The current onset will be used as an indicative of the feasibility of the deposition process under the different electrodeposition conditions and as a comparison tool between the behaviour of the different solutions. In none condition, oxidation current related to aluminium oxidation was recorded in the positive scan.

The electrodeposition of aluminium from the employed solutions at 100ºC was investigated with the objective of getting thick and adherent deposits on nickel. The chronoamperometric experiments were done by switching the potential to the selected value from a potential of 0.4V, at which no process occurs. Applied potentials were selected according to the corresponding voltammetric curves. The recorded potentiostatic curves show similar behaviour, in which a monotonic current increase was noticed as the deposition time passed. Experiments at the most negative potentials applied lead to j-t transients that developed a maximum, after which the current decreases (Fig. 7D). The higher the negative potential is, the faster transition.

Aluminium deposits were prepared from the 1.2:1 $AlCl_3$-IL solutions using potentiostatic technique. The SEM images of prepared deposits at moderate overpotential show that the substrate was completely covered (Fig. 8A), but increasing the applied charge, some tensions are evident (Fig. 8B). The deposition potential should be carefully considered, since a high deposition rate brings out loose structure (Fig. 8C). The deposits are more stressed, as the applied potential was more negative and longer the deposition time. Using GUA lower overpotentials were applied according to voltammetric results. In the supporting information different SEM images of deposits obtained from GUA ionic liquid illustrating that for the deposits prepared at soft deposition conditions incipient cracks appear (Fig. S5A and B). Incipient tensions were also detected in the deposits prepared using IMI at moderate overpotentials (Fig. S5C).

The EDS elemental analysis confirmed the aluminium deposition (Fig. 8D), due to the discrete thickness of prepared deposits, the presence of nickel substrate was evident.

Modifying the electrodeposition conditions, even promoting moderate current rates, it was not possible to obtain stress-free deposits, except by applying very low overpotentials, conditions that lead to obtain very thin deposits and were highly time consuming. Therefore, chronopotentiometry was checked as alternative preparation technique: Chronopotentiometric technique promotes nucleation more easily, fact that could favour the growth of the deposits in a homogeneous way. The voltammetric response was also used, as a reference, to select the appropriate currents.

The chronopotentiometric curves recorded show a potential evolution, coherent to nucleation and growth processes (Fig. 9A). At first, the potential drops to a minimum value, and afterwards monotonically increases over time to the potential needed to achieve the demanded current at stationary conditions. Figure 9A includes the first deposition times of three curves that show the general behaviour. As current increases, the spike potential attains a more negative value and appears sooner. Visually the deposits obtained seem uniform and well attached, covering the entire substrate. The characterization of the deposits by SEM confirms that are coherent (Fig. 9B) being formed by a compact layer that sporadically shows little ball-like agglomerates on the surface (Fig. 9C). Increasing the applied current density, the deposits turn out slightly stressed (Fig. 9D), and several cracks could be found within. Visual and SEM imaging demonstrate that this preparation method improves the quality of the deposits in comparison to those prepared potentiostaticaly under similar conditions.

3.3.3 Influence of concentration and temperature

The effect of different electrodeposition conditions, such as temperature, applied current and $AlCl_3$:IL molar ratio was analysed in a temperature range between 95 and 130ºC using $AlCl_3$:GUA solutions between 0.95:1 and 1.3:1 molar ratios.

Figure 10A contains the cyclic voltammograms recorded at different temperatures showing that the onset of deposition potential shifts to less negative values with the increase of temperature as it was expected. On the other hand, voltammetric experiments performed at fixed temperature from solutions of different concentration evidenced that the lower the molar ratio is, the lower the voltammetric current onset potential (Fig. 7B).

Deposits were prepared under constant current conditions. The galvanostatic curves associated with the deposit preparation show that in experiments performed at fixed both temperature and $AlCl_3$:GUA molar ratio, the deposition process occurred at higher overpotential as greater is the demanded current density. From the same solution and applied current, the minimum potential achieved was more negative as the temperature decreases (Fig. 10B). For the lowest temperature (95ºC) the galvanostatic curves show similar profile, at first the potential drops to the value of nucleation spike, increasing afterwards to stationary value as is predictable but after certain deposition time the potential decreases. This later decrease of the potential value is probably related to the higher viscosity of the solution, associated to the low work temperature, that could difficult the contribution of electroactive species to the electrode.

Deposits prepared at different $AlCl_3$:GUA molar ratios and temperatures show drastic changes in the surface morphology, as a result of variations in the electrodeposition conditions, current

density, Al(III) content and temperature. From the solution with the lower Al(III) concentration, AlCl$_3$:GUA 0.95:1 molar ratio, stress-free deposits were obtained even at temperature of 110ºC (Fig. 11 A and B), rising temperature, deposits show little cracks (Fig. 11C), more evident at 130ºC (Fig. 11D). So, at the low AlCl$_3$ concentration, adherent and stress-free deposits could be prepared at moderate applied currents when temperature is no higher than 110ºC. The morphology shows that the prepared deposits are coherent but not homogenous in thickness, possibly due to the low electroactive concentration.

Using the most concentrated solution AlCl$_3$:GUA at 1.3:1 molar ratio and moderate applied current densities at the lowest temperature checked (95ºC), coherent and continuous crack-free deposits were obtained (Fig. 12A), whereas the rise of temperature to 110ºC lead to some scattered cracks on the aluminium surface (Fig. 12B), that are not present reducing the demanded current (Fig. 12C). From this solution, experiments above 110ºC lead to looser deposits (Fig. 12D). On the other hand, for all temperatures, the higher the applied current is, the higher stress observed. Thus, from this AlCl$_3$:GUA solution the best quality deposits, according uniformity, morphology and adherence were obtained at the lowest temperature tested, 95ºC in a wide applied current range with reasonable time consuming. The preparation conditions at low temperature and high concentration favour the formation of useful aluminium deposits and open the possibilities to prepare Al coherent deposits in ambient.

4. Conclusions

New ionic liquids designed by Solvay as solvents for aluminum electrodeposition were investigated. The three liquids are water- and air-stable, prepared with the new synthetized anion perfluoro-3-oxa-4,5-dichloro-pentan-sulphonate [CF$_2$ClCFClOCF$_2$CF$_2$SO$_3^-$], that enhances high hydrophobicity. The new liquids dissolve Al(III) independently whether the Al(III) source was Al(OH)$_3$ or AlCl$_3$ and permit to work in ambient system.

Vitreous carbon was used to evaluate the feasibility of aluminium deposition. Using Al(OH)$_3$ flaked deposits were obtained, similar to the ones observed using less fluorinated liquids, whereas from AlCl$_3$ coherent, continuous and fine-grained deposits were prepared. Nickel was chosen as metallic substrate, it was forced to discard copper because AlCl$_3$:ILs solutions promote its chemical attack.

The use of PYR was not considered because it is only possible to obtain true solutions at moderate concentration. This evidences the great influence that the counterion exerts in these ionic liquids, inducing severe changes in the properties of the Al(III) solutions.

Cyclic voltammetry was used as characterization tool of the electrochemical process and potentiostatic and galvanostatic techniques for the preparation of deposits. At low deposition times, the characteristic features of nucleation and growth process were observed from the three electrochemical techniques, confirming the aluminium deposition. The general behaviour for the employed ionic liquids, imidazolium and guanidinium, was similar, regardless small differences in the onset of deposition potentials.

Deposits prepared on nickel under constant potential show some stress, with cracks distributed randomly on the surface, more evident when the deposit is thick enough. The progressive nucleation in this media generates stress. Hence, the deposits were prepared at constant current that promotes easy nucleation and reduces the stress of the prepared deposits.

As not relevant differences in the characteristics of the electrodeposits were noticed using the two liquids, the temperature effect was analysed using GUA. This selection was performed taking advantage of the total immiscibility in water of the GUA liquid, relevant factor that would improve the use of this bath in an open system in future applications.

Obtained deposits display changes, making evident that the deposition process is very sensitive to the concentration of the solution, temperature and applied current. Tailoring preparation conditions is possible to obtain crack-free deposits. At this stage, we have established that a convenient combination of parameters is necessary in order to control the Al(III) reduction process. The mastering of variable effects can lead to the formation of quality aluminum coatings together with an enhancement of the deposition rates.

With these ionic liquids, especially with GUA, it has been proved that the preparation of aluminium deposits would need less stringent environmental conditions than with other less hydrophobic liquids. The use of these novel liquids maintains the stability of the electroactive solutions.

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Captions for figures

Figure 1.- Conductivity values at different temperatures for: a) GUA , b) IMI and c) PYR ionic liquids.

Figure 2.-Voltametric curves from the ionic liquids at 100ºC at 10 mV s^{-1}: a) GUA,˙ b) IMI and c) PYR. Nickel electrode.

Figure 3.-Chronopotentiometric curves recorded at 100ºC from GUA ionic liquid at: a) 50, b) 25, c) 10, d) -10, e) -25 and f) -50 µA cm^{-2}. Nickel electrode.

Figure 4.- For the 0.9:1, Al(OH)$_3$: GUA molar ratio solution at 100ºC: A) Voltammetric curves at 10 mVs^{-1}. B) j-t transients recorded at different applied potentials: a) -0.50, b) -0.55 and c) -0.60 V. SEM images of deposits obtained at: C) 0.53 V and D) 0.58 V. Vitreous carbon electrode.

Figure 5.- Voltammetric curves at 10 mVs^{-1} recorded at 100ºC from: A) the 1.1:1, AlCl$_3$: PYR molar ratio solution at different reverse potentials, B) the 1:1, AlCl$_3$: IMI molar ratio solution, consecutive scans a) first, b) second scan. Vitreous carbon electrode.

Figure 6.- A) j-t transients recorded for 1:1 AlCl$_3$: IMI molar ratio solution at different applied potentials: a) -0.50, b) -0.55 and c) -0.59 V. SEM images of deposits obtained from 1.1:1 AlCl$_3$: PYR molar ratio solution at: B) -0.35, C) -0.40 and D) 0.50 V. Temperature 100ºC and vitreous carbon electrode. Q = -50mC.

Figure 7.- A) Voltammetric curve recorded at 10 mVs^{-1} from the 1.2:1, AlCl$_3$: GUA molar ratio solution, B) Voltammetric curves recorded at 10 mVs^{-1} from a) 1.3:1, b) 1.1:1 and c) 0.95:1 AlCl$_3$: GUA molar ratio solutions, C) Voltammetric curves recorded at 10 mVs^{-1} from 1.2:1 molar ratio solutions of: a) AlCl$_3$: GUA and b) AlCl$_3$: IMI, and D) j-t transients recorded for 1.2:1 AlCl$_3$: IMI molar ratio solution: a) -0.25 V and b) -0.37 V. Temperature 100ºC and nickel electrode.

Figure 8.- SEM images of deposits obtained potentiostaticaly at 100ºC from the 1.2:1, AlCl$_3$: IMI molar ratio solution at: A) -0.25 V and Q = -300 mC, B) -0.25 V and Q = -900 mC, and C) -0.37 V and Q = -500 mC. D) EDS analysis. Nickel electrode.

Figure 9.- From 1.2:1, AlCl$_3$: IMI molar ratio solution A) Chronopotentiograms at: a) 1.5, b) 2 and c) 2.5 mA cm^{-2}. SEM images of deposits obtained at: B) -1.5 mA cm^{-2} , Q = -500 mC, C) detail of B and D) -3 mA cm^{-2}, Q = -800 mC. Temperature 100ºC and nickel electrode.

Figure 10.- A) Voltammetric curves recorded at 10 mVs^{-1} from the 0.95:1, AlCl$_3$: GUA molar ratio solution, at temperature of: a) 100ºC, b) 110ºC and c) 120ºC. B) Chronopotentiograms

from the 1.30:1, $AlCl_3$: GUA molar ratio solution at 1 mA cm^{-2} at different temperatures: a) 130, b) 120 and c) 110 and d) 95ºC. Nickel electrode.

Figure 11.- SEM images of deposits obtained from the 0.95:1, $AlCl_3$: GUA molar ratio solution at 2 mA cm^{-2} at different temperatures: A) 100ºC, B) 110ºC C) 120ºC and D) 130ºC. Nickel electrode.

Figure 12.- SEM images of deposits obtained from the 1.3:1, $AlCl_3$: GUA molar ratio solution at 2 mA cm^{-2} at different temperatures: A) 95ºC, inset at higher magnification, B) 110ºC, inset at higher magnification. C) 110ºC at 1.5 mA cm^{-2} and D) -120ºC. Nickel electrode.

Electrodeposition of Aluminium from hydrophobic perfluoro-3-oxa-4,5 dichloro-pentan-sulphonate based ionic liquids

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Abstract

Aluminium electrodeposition from ionic liquids (ILs) prepared using a novel structure composed by perfluoro-3-oxa-4,5 dichloro-pentan-sulphonate $[CF_2ClCFClOCF_2SO_3^-]$ and different cations is presented. The novel anion was designed by Solvay Specialty Polymers with the purpose to confer to the ionic liquids strong hydrophobic properties that facilitate the aluminium deposition in ambient conditions. Three cations, imidazolium, pyridinium and guanidinium are used to prepare the corresponding three liquids. In water, the resulting liquids prepared with imidazolium and pyridinium show very low miscibility and the liquid prepared with guanidinium is insoluble. Their electrochemical windows are dependent of both the cations and the substrate nature and are sufficiently wide to allow aluminium deposition. Even so, it was evidenced that the reduction of the new structure is not especially difficult. The $AlCl_3$ was selected as useful source of Al(III) electroactive species to obtain coherent deposits. Using aluminium hydroxide, the coalescence of the aluminium deposits was not achieved.

The viability of aluminium electrodeposition was, at first, tested on vitreous carbon, demonstrating it follows through a nucleation and growth process. As the practical interest carries to the use of metallic substrata, nickel was selected to analyse deposition process. The deposits prepared at constant current showed a better appearance, less stressed and smoother than the ones prepared at constant potential. The effect of temperature and concentration was studied in solutions prepared with tetramethyl guanidinium-perfluoro-3-oxa-4,5 dichloro-pentan-sulphonate, taking advantage of its immiscibility in water. Deposits prepared from the lower concentrations tested ($AlCl_3$:IL 0.95:1 molar ratio) were continuous, fine grained and stress-free, provided that they were obtained at moderate applied current. From higher Al(III) concentration solutions it was only possible to allow stress-free deposits by applying low currents.

Keywords: aluminium electrodeposition, hydrophobic ionic liquid, vitreous carbon substrate, nickel substrate, open-air system

1. Introduction

Lately the plating of aluminium (Al) has been widely investigated due to its potential applications (both aesthetic and functional) including corrosion protection [1, 2], decorative coatings [3], electrorefining processes [4, 5], electronics [6], and current collectors in Al-ion

batteries [7-9]. Applications that have an important industrial role due to the low cost, low density and environmentally benign nature of aluminium.

Much research has been done on several methods for the preparation of aluminium deposits. Among those currently available are electrodeposition, thermal processing (thermal spray coating and hot dipping) [10-13], or low pressure vapour phase deposition, PVD [14] and CVD [15]. However, some of these methods are quite expensive, technically demanding and do not permit obtaining thin films.

In fact, electrodeposition is the preferred method as it is simple, cost-efficient, has low energy consumption, can be used on objects with complex shapes and implies relatively easy control. Unfortunately, given the low standard potential of Al(III)/Al couple, the use of aqueous baths for aluminium deposition is unsuitable. Therefore, aluminium electrodeposition has been carried out using either organic solvents [16-19] or inorganic molten salts [20], but both kinds of solutions present strong limitations related to their flammability and corrosive action. Such drawbacks have led to study the possibility of using Ionic Liquids (ILs) as electrochemical media for aluminium electrodeposition since they do show some promising results.

In the past two decades, numerous groups have studied the electrodeposition of aluminium using ionic liquids. ILs show attractive physicochemical properties, including a wide electrochemical window (that can be tailored by modifying the ionic components), low vapour pressure, high intrinsic conductivities, moderate viscosities and high boiling point that make them also, environmentally friendly. Most of the work related to aluminium electrodeposition in ionic liquids has been done using chloroaluminate ILs (the so-called first generation ILs), in which the $[Al_2Cl_7]^-$ complex formed in the Lewis acidic melt can be reduced to metallic aluminium [21, 22]. Plating solutions are easy to prepare by simple addition of the Lewis acid $AlCl_3$ to N,N´-dialkyl-imidazolium chloride [23-32], alkyl-pyridinium chloride [33], N-alkylpyrrolidinium [34, 35] or to quaternary ammonium compounds [36, 37] under an inert atmosphere. Such media are, however, moisture sensitive and the solutions require strictly controlled conditions. A second class of liquids was subsequently developed (known as air-and water stable ILs) which presented an improved hydrophobicity due to their particular anionic structures. Some of them are tetrafluoroborate (BF_4^-), trifluoromethylsulfonate (CF_3SO_3-), bis(trifluoromethylsulfonyl)-imide $[(CF_3SO_2)_2N^-]$, and tris(trifluoromethylsulfonyl)methide $[(CF_3SO_2)_3C^-]$. While aluminium was deposited using these liquids [38-41], it was found that long exposures to temperature and atmospheric humidity could change their physicochemical properties [42]. For these reasons, these solutions needed to be used under inert atmosphere in order to prevent degradation.

From the aforementioned problems, it can be easily understood that the industrial processing of aluminium electrodeposition has still not been well mastered, and the finding of a moisture-resistant route to aluminium electrodeposition remains still to be found.

Recently different proposals have been put forward in order to solve the technological problems of aluminium deposition. Thus, researchers proposed the possibility of electrodepositing functional aluminium layers from an $AlCl_3$/ionic liquid in ambient conditions, by insulating the electrolyte from air with a layer of a specific hydrocarbon compound [43, 44] and this did indeed enable aluminium to be deposited outside the glove box. Other alternatives proposed involve the use of $AlCl_3$-based ionic liquids with a neutral substituted ligand. Such liquids have been prepared using group V nitrogen-based ligands. Recently, since group VI elements possess also single electron pair, Al-ILs based on ligands with O and S have been introduced and investigated. These new ILs based on complexation with neutral ligands are formed by interaction between the ligands and $AlCl_3$, to produce Al-containing ions by the asymmetric cleavage of $AlCl_3$.

The liquids prepared differ fundamentally from first generation ones, since the positive charge is placed on the aluminium, whereas in the previous ones the electroactive species were negative. This can be beneficial as the electroactive cationic metal complexes can easily reach electrode surface. Abbott et al. [45] reported that simple neutral amides (acetamide and urea) could be mixed with $AlCl_3$ to form room-temperature ILs, which have been used for aluminium electrodeposition. These ILs however, cannot shield effectively the aluminium centre and, consequently, are still moisture sensitive. Alternatively, new proposals involving complexing agents containing aromatic rings are being analysed with the idea that the ring's presence could mitigate moisture sensitivity [46-49]. The development of such ILs using readily available and relatively hydrophobic "neutral" ligands could be of great interest for the practical electroplating of aluminium.

It is known that both chain length and nature of the anion in the ionic liquid have an influence on electrochemical behaviour. Considering this united to the fact that the hydrophobicity of the IL is specific of the anionic structure, the present work is focused on systems in which the anion hydrophobicity has been enhanced as a possible way to overcome the Achilles' heel of aluminium electrodeposition in open systems. For this, the use of new perfluoroalkyl sulfonate salts has been developed and studied in collaboration with the R&D centre of Solvay Specialty Polymers, which possess high expertise in fluorinated products and organic synthesis. In this work we present results obtained with three ionic liquids prepared combining an innovative anion, perfluoro-3-oxa-4,5 dichloro-pentan sulphonate $[CF_2ClCFClOCF_2CF_2SO_3]$, with three

different conventional cations: N,N-dimethyl imidazolium (IMI as acronym of the liquid), tetramethyl guanidinium (GUA as acronym of the liquid) and 1,2,4,6-tetramethyl pyridinium (PYR as acronym of the liquid). These products lead to water- and air stable ionic liquids even after adding the aluminium source, being interesting systems for the study of aluminium plating in an open system.

In a previous work, an exhaustive study was performed on vitreous carbon substrate using GUA as solvent [50], in which aluminium electrodeposition was demonstrated in a wide range of $AlCl_3$:IL molar ratios. This work focuses on the study of aluminium deposition process from liquids in which the hydrophobic character was enhanced, extending the analysis to metallic substrates, because the final technological interest is the deposition on polymeric substrates functionalized with metallic seed layer. Aluminium electroplating from $AlCl_3$ on vitreous carbon was checked from solutions prepared with PYR and IMI. The possibility to deposit from aluminium hydroxide as a source of electroactive Al(III) species was also explored. Deposition on metallic substrates was carried out under different potentiostatic and/or galvanostatic conditions. The prepared deposits were characterized using scanning electron microscopy. The influence of some electrodeposition conditions like Al(III) concentration and temperature was analysed.

2. Experimental

The behaviour of three novel ILs sharing the same anion perfluoro-3-oxa-4,5-dichloro-pentan-sulphonate [$CF_2ClCFClOCF_2CF_2SO_3^-$], N,N-dimethyl imidazolium (IMI), tetramethyl guanidinium (GUA) and 1,2,4,6-tetramethyl pyridinium (PYR) supplied by Solvay Specialty Polymers, was studied. Blank solutions were prepared by melting a weighted amount of IL using a silicone bath under inert atmosphere and stirring conditions. The melting points of the liquids are for IMI 56°C, for GUA 71°C and for PYR 78°C. In water, GUA is insoluble and IMI and PYR show very low solubility.

Conductivity was measured at different temperatures using a Metrohm 644 conductometer with a 52-92 Crison^{TM} conductivity cell (1 cm^{-1} of cell constant). The cell contained two parallel platinum sheets, the temperature was controlled with an accuracy of 0.3°C using a Pt (100 ohm) resistor from Kosmon.

The electroactive solutions were prepared by dissolving the pertinent aluminium reactant, in the IL following the protocol: The weighed amount of IL was melted in nitrogen atmosphere in a Schlenk flask. Once liquefied the IL, the weighed amount of $Al(OH)_3$ (from Cymit) or $AlCl_3$ (from Sigma-Aldrich) was added to obtain the desired Al(III):IL molar ratio. $Al(OH)_3$ and

AlCl$_3$ dissolve well and homogeneously although slowly in the ILs under stirring and heating at 100ºC. The appearance of the solutions was different in each case, being caramel-like in AlCl$_3$-GUA, white and thick in AlCl$_3$-IMI and yellowish in AlCl$_3$-PYR, whereas all solutions obtained from Al(OH)$_3$ were white. Using PYR was necessary moderate agitation, otherwise a gum ball was formed. Solutions with concentration lower than 0.9:1 Al(III):IL were not considered according to the previous results obtained [50].

The electrochemical study was carried out using an Autolab with PGSTAT30 equipment and GPES software. A thermostatically-controlled three electrode open cell of a single compartment was used. Working electrodes were glassy carbon rod of 2 mm of diameter from Metrohm or small sheets (effective area 0.25 cm^2) of nickel or copper from John Matthey. The glassy carbon was polished to mirror finish using alumina of different grades (3.75 and 1.87 µm), cleaned ultrasonically for 2 min in water and dried with air prior to be immersed in the solution. Using nickel or copper as working electrodes, they were dipped in a solution of nitric acid (1:1) and afterwards polished with alumina 1.87 µm. Aluminium and platinum wires were used as pseudo-reference and counter electrodes respectively. Aluminium wire was mechanically polished with Struers SiC 4000 paper and platinum wire was heated in a flame to incandescence during several minutes after immersion in a nitric acid solution (1:1). Water remained was removed with nitrogen flow prior to the immersion of electrodes in the solution.

Voltammetric experiments were performed at scan rate of 10 mVs^{-1}, in favour of recording accurate curves. The experiments were done scanning first to negative potentials. Chronoamperometric experiments were performed starting from a potential were no process took place and jumping to the selected potential value. Galvanostatic curves were recorded at different currents selected according previous voltammetric results. Deposits were prepared by means of potentiostatic and galvanostatic techniques and after were quickly removed from the solution and carefully washed, first in warm dichloromethane, then in a dichloromethane-acetone mixture and finally in acetone.

Experiments were made using fresh substrates and the working temperature was 100ºC unless otherwise stated.

A scanning electron microscope Field Emission JSM-7100F Analytical Microscopy was used to study the morphology of the films. Energy dispersive X-ray analysis allowed to determine the elemental composition of the deposits.

3. Results and discussion

3.1. Ionic liquids characterization

The conductivity of the ILs was measured, from their melting temperature up 120ºC in order to get information about adequate work temperature range. As observed previously for GUA [50], an increase of the temperature leads to a rise in the conductivity (Fig.1), being the values for IMI and PYR slightly higher than those measured for GUA.

Due to the intrinsic high melting temperature of the ILs, the electrochemical experiments were performed at 100ºC, in order to assure reasonable conductivity for the future deposition purpose. The voltammetric window was established using three different working electrodes, vitreous carbon, nickel and copper, starting at potential values at which current did not appear and scanning towards negative potential values. Figure 2 shows the recorded voltammetric profiles on nickel substrate.

The comparison between the three substrates (Fig. S1) shows that the appearance of the massive reduction current is directly linked to the nature of the substrates. Reversing the scan some reduction current was maintained along the positive scan. Copper is the substrate with the narrowest electrochemical window, starting the oxidation at around 0V, related to substrate oxidation. The electrochemical windows are dependent on the temperature, lowering the working temperature the effective window was widened, as was observed for GUA liquid [50].

As an alternative characterization test of these synthetized ionic liquids, the interest was centred on the evolution of the potential value under different current demand, as a tool to ascertain the feasibility of oxidation (reduction) of these liquids on the selected substrates. Currents were lead to both positive and negative values with the purpose of evaluating the easiness of the reduction (oxidation) processes.

Figures 3 and S2 show the chronopotentiometric responses corresponding to the demand on quiescent conditions of six different current densities, three negative and three positive for GUA and PYR on nickel substrate. In order to achieve the demanded current, the potential value evolves to a more negative (positive) potential, depending on both the sign and the current value. Increasing the time the potential tends to quasi-stationary value, more negative (positive) as the negative (positive) demanded current has higher absolute value. On these liquids, the general trend shows that, the differences between the corresponding stationary potential values achieved for the positive demanded currents were greater than for the negative

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ones. Greater easiness was observed for the reduction process than for the corresponding oxidation. The selected counter cations seem less electroactive than the synthetized anion. Similar general behaviour was observed from GUA on vitreous carbon [50].

3.2. Aluminium deposition from Al(OH)$_3$

Due to the novelty of the anion two possible sources for Al(III) electroactive species were analysed, aluminium hydroxide (Al(OH)$_3$) and aluminium chloride (AlCl$_3$).

The feasibility of deposition using aluminium hydroxide was demonstrated by electrochemical results and imaging analysis. The voltammetric curves recorded on vitreous carbon show a small band before a sudden increase in the reduction current (Fig. 4A). The Al-deposition was proposed after the recording of the typical current nucleation loop observed when reversing the scan in the potential zone related to the sudden current increase (inset Fig. 4A) [51]. However, current loop was not recorded reversing the scan in the potential zone of the first band.

Although the aluminium reduction occurs, the imaged deposits obtained potentiostaticaly at different conditions trough j-t transients similar to those in Fig. 4B, show that the deposits were non-coherent and lack of compactness. At low overpotentials are porous and seem spongy (Fig. 4C, S3A), while the obtained at high overpotentials are constituted by blocks or sheets distributed randomly along the substrate (Fig. 4D, S3B). Modifying the electrodeposition conditions it was not possible to get enough improvement in the quality of deposits from this aluminium source.

Attending these preliminary results, the use of aluminium hydroxide was abandoned and the efforts were focused on the deposition process using AlCl$_3$ as electroactive species source.

3.3. Aluminium deposition from AlCl$_3$

After soaking the copper substrate in the prepared AlCl$_3$:IL solutions from the three liquids, chemical attack on copper surface was observed, reason that forced to discard its use as substrate. This chemical attack was especially evident when the tested substrate was a very thin copper layer deposited over flexible polymer (Fig. S4).

3.3.1 Electrodeposition on vitreous carbon

At first the objective was to trace the feasibility of aluminium deposition on vitreous carbon from AlCl$_3$ solutions (AlCl$_3$:IL 1.1:1 molar ratio) prepared using IMI and PYR ionic liquids, as previously demonstrated using GUA as solvent [50]. For both solutions the voltammetric features were similar. Figure 5A shows the voltammograms recorded at different negative limits, in which can be observed that, a current band (C$_1$) appears previous to sudden current

increase. In the inset of the figure 5A, it can be appreciated that reversing the scan in the C_1 potential range, a nucleation current loop does not appear. The process involved in the C_1 band is not related to new phase formation. Elonging the scan a peak/shoulder C_2 was developed. Figure 5B shows two consecutive voltammograms, in which the appearance of the nucleation loop after reversing the scan in the potential zone of C_2 peak (Fig. 5B curve a) evidences that a new phase is formed by nucleation and growth mechanisms at more negative potentials than those of C_1 band. The advancement of the onset of the current appearance in the second scan (Fig. 5B curve b) evidences that the process takes place on favoured conditions, on freshly deposited aluminium. Altogether it indicates that the bulk deposition of aluminium from these solutions occurs.

Aluminium deposits were prepared at constant potential under a regime in which monotonic current increase was observed in the recorded j-t transients, confirming newly the feasibility of aluminium deposition from these $AlCl_3$:IL solutions (Fig. 6A). The deposits prepared at low overpotentials show nodular morphology (Fig. 6B) with rounded grains similar to the previous one obtained from GUA [50]. Imaging the deposits prepared at more negative potentials, a grain reduction was observed (Fig. 6C), but increasing the overpotential, very stressed deposits were obtained, for which the grain was hardly recognizable (Fig. 6D). Increasing the $AlCl_3$:IMI molar ratio, similar behaviour was observed. Nevertheless, the preparation of solutions of higher $AlCl_3$ concentrations using pyridinium (PYR) was not feasible, because rubber-like ball-aggregates were formed.

3.3.2 Electrodeposition on nickel

Due to the problems involved in the preparation of the solutions using PYR, onwards the aluminum deposition study on nickel was restricted to IMI and GUA solvents.

Voltammetric experiments conducted on nickel substrate exhibit quite a similar behaviour for both kind of solutions. The voltammetric C_1 band observed on vitreous was not detected, and elonging the scan the sudden current increase related to bulk deposition moderates and shows the appearance of an incipient reduction peak (Fig. 7A). Figure 7B shows the cyclic voltammograms recorded from three different $AlCl_3$:GUA molar ratios, the reduction current appears at less negative potentials increasing the $AlCl_3$:IL molar ratio. The typical nucleation loop appears after reversing the scan at moderate overpotentials (Fig. 7B curves a and b). The presence of a clear reduction peak related with a certain mass control is evident for the lower $AlCl_3$:IL molar ratio investigated (Fig.7B curve c). Figure 7C shows the voltammograms obtained at similar conditions from solutions prepared from the two solvents, evidencing that

the aluminium deposition process is slightly more favourable in the solution prepared using guanidinium. The current onset will be used as an indicative of the feasibility of the deposition process under the different electrodeposition conditions and as a comparison tool between the behaviour of the different solutions. In none condition, oxidation current related to aluminium oxidation was recorded in the positive scan.

The electrodeposition of aluminium from the employed solutions at 100ºC was investigated with the objective of getting thick and adherent deposits on nickel. The chronoamperometric experiments were done by switching the potential to the selected value from a potential of 0.4V, at which no process occurs. Applied potentials were selected according to the corresponding voltammetric curves. The recorded potentiostatic curves show similar behaviour, in which a monotonic current increase was noticed as the deposition time passed. Experiments at the most negative potentials applied lead to j-t transients that developed a maximum, after which the current decreases (Fig. 7D). The higher the negative potential is, the faster transition.

Aluminium deposits were prepared from the 1.2:1 $AlCl_3$-IL solutions using potentiostatic technique. The SEM images of prepared deposits at moderate overpotential show that the substrate was completely covered (Fig. 8A), but increasing the applied charge, some tensions are evident (Fig. 8B). The deposition potential should be carefully considered, since a high deposition rate brings out loose structure (Fig. 8C). The deposits are more stressed, as the applied potential was more negative and longer the deposition time. Using GUA lower overpotentials were applied according to voltammetric results. In the supporting information different SEM images of deposits obtained from GUA ionic liquid illustrating that for the deposits prepared at soft deposition conditions incipient cracks appear (Fig. S5A and B). Incipient tensions were also detected in the deposits prepared using IMI at moderate overpotentials (Fig. S5C).

The EDS elemental analysis confirmed the aluminium deposition (Fig. 8D), due to the discrete thickness of prepared deposits, the presence of nickel substrate was evident.

Modifying the electrodeposition conditions, even promoting moderate current rates, it was not possible to obtain stress-free deposits, except by applying very low overpotentials, conditions that lead to obtain very thin deposits and were highly time consuming. Therefore, chronopotentiometry was checked as alternative preparation technique: Chronopotentiometric technique promotes nucleation more easily, fact that could favour the growth of the deposits in a homogeneous way. The voltammetric response was also used, as a reference, to select the appropriate currents.

The chronopotentiometric curves recorded show a potential evolution, coherent to nucleation and growth processes (Fig. 9A). At first, the potential drops to a minimum value, and afterwards monotonically increases over time to the potential needed to achieve the demanded current at stationary conditions. Figure 9A includes the first deposition times of three curves that show the general behaviour. As current increases, the spike potential attains a more negative value and appears sooner. Visually the deposits obtained seem uniform and well attached, covering the entire substrate. The characterization of the deposits by SEM confirms that are coherent (Fig. 9B) being formed by a compact layer that sporadically shows little ball-like agglomerates on the surface (Fig. 9C). Increasing the applied current density, the deposits turn out slightly stressed (Fig. 9D), and several cracks could be found within. Visual and SEM imaging demonstrate that this preparation method improves the quality of the deposits in comparison to those prepared potentiostaticaly under similar conditions.

3.3.3 Influence of concentration and temperature

The effect of different electrodeposition conditions, such as temperature, applied current and $AlCl_3$:IL molar ratio was analysed in a temperature range between 95 and 130ºC using $AlCl_3$:GUA solutions between 0.95:1 and 1.3:1 molar ratios.

Figure 10A contains the cyclic voltammograms recorded at different temperatures showing that the onset of deposition potential shifts to less negative values with the increase of temperature as it was expected. On the other hand, voltammetric experiments performed at fixed temperature from solutions of different concentration evidenced that the lower the molar ratio is, the lower the voltammetric current onset potential (Fig. 7B).

Deposits were prepared under constant current conditions. The galvanostatic curves associated with the deposit preparation show that in experiments performed at fixed both temperature and $AlCl_3$:GUA molar ratio, the deposition process occurred at higher overpotential as greater is the demanded current density. From the same solution and applied current, the minimum potential achieved was more negative as the temperature decreases (Fig. 10B). For the lowest temperature (95ºC) the galvanostatic curves show similar profile, at first the potential drops to the value of nucleation spike, increasing afterwards to stationary value as is predictable but after certain deposition time the potential decreases. This later decrease of the potential value is probably related to the higher viscosity of the solution, associated to the low work temperature, that could difficult the contribution of electroactive species to the electrode.

Deposits prepared at different $AlCl_3$:GUA molar ratios and temperatures show drastic changes in the surface morphology, as a result of variations in the electrodeposition conditions, current

density, Al(III) content and temperature. From the solution with the lower Al(III) concentration, AlCl$_3$:GUA 0.95:1 molar ratio, stress-free deposits were obtained even at temperature of 110ºC (Fig. 11 A and B), rising temperature, deposits show little cracks (Fig. 11C), more evident at 130ºC (Fig. 11D). So, at the low AlCl$_3$ concentration, adherent and stress-free deposits could be prepared at moderate applied currents when temperature is no higher than 110ºC. The morphology shows that the prepared deposits are coherent but not homogenous in thickness, possibly due to the low electroactive concentration.

Using the most concentrated solution AlCl$_3$:GUA at 1.3:1 molar ratio and moderate applied current densities at the lowest temperature checked (95ºC), coherent and continuous crack-free deposits were obtained (Fig. 12A), whereas the rise of temperature to 110ºC lead to some scattered cracks on the aluminium surface (Fig. 12B), that are not present reducing the demanded current (Fig. 12C). From this solution, experiments above 110ºC lead to looser deposits (Fig. 12D). On the other hand, for all temperatures, the higher the applied current is, the higher stress observed. Thus, from this AlCl$_3$:GUA solution the best quality deposits, according uniformity, morphology and adherence were obtained at the lowest temperature tested, 95ºC in a wide applied current range with reasonable time consuming. The preparation conditions at low temperature and high concentration favour the formation of useful aluminium deposits and open the possibilities to prepare Al coherent deposits in ambient.

4. Conclusions

New ionic liquids designed by Solvay as solvents for aluminum electrodeposition were investigated. The three liquids are water- and air-stable, prepared with the new synthetized anion perfluoro-3-oxa-4,5-dichloro-pentan-sulphonate [CF$_2$ClCFClOCF$_2$CF$_2$SO$_3^-$], that enhances high hydrophobicity. The new liquids dissolve Al(III) independently whether the Al(III) source was Al(OH)$_3$ or AlCl$_3$ and permit to work in ambient system.

Vitreous carbon was used to evaluate the feasibility of aluminium deposition. Using Al(OH)$_3$ flaked deposits were obtained, similar to the ones observed using less fluorinated liquids, whereas from AlCl$_3$ coherent, continuous and fine-grained deposits were prepared. Nickel was chosen as metallic substrate, it was forced to discard copper because AlCl$_3$:ILs solutions promote its chemical attack.

The use of PYR was not considered because it is only possible to obtain true solutions at moderate concentration. This evidences the great influence that the counterion exerts in these ionic liquids, inducing severe changes in the properties of the Al(III) solutions.

Cyclic voltammetry was used as characterization tool of the electrochemical process and potentiostatic and galvanostatic techniques for the preparation of deposits. At low deposition times, the characteristic features of nucleation and growth process were observed from the three electrochemical techniques, confirming the aluminium deposition. The general behaviour for the employed ionic liquids, imidazolium and guanidinium, was similar, regardless small differences in the onset of deposition potentials.

Deposits prepared on nickel under constant potential show some stress, with cracks distributed randomly on the surface, more evident when the deposit is thick enough. The progressive nucleation in this media generates stress. Hence, the deposits were prepared at constant current that promotes easy nucleation and reduces the stress of the prepared deposits.

As not relevant differences in the characteristics of the electrodeposits were noticed using the two liquids, the temperature effect was analysed using GUA. This selection was performed taking advantage of the total immiscibility in water of the GUA liquid, relevant factor that would improve the use of this bath in an open system in future applications.

Obtained deposits display changes, making evident that the deposition process is very sensitive to the concentration of the solution, temperature and applied current. Tailoring preparation conditions is possible to obtain crack-free deposits. At this stage, we have established that a convenient combination of parameters is necessary in order to control the Al(III) reduction process. The mastering of variable effects can lead to the formation of quality aluminum coatings together with an enhancement of the deposition rates.

With these ionic liquids, especially with GUA, it has been proved that the preparation of aluminium deposits would need less stringent environmental conditions than with other less hydrophobic liquids. The use of these novel liquids maintains the stability of the electroactive solutions.

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Captions for figures

Figure 1.- Conductivity values at different temperatures for: a) GUA , b) IMI and c) PYR ionic liquids.

Figure 2.-Voltametric curves from the ionic liquids at 100ºC at 10 mV s^{-1}: a) GUA, b) IMI and c) PYR. Nickel electrode.

Figure 3.-Chronopotentiometric curves recorded at 100ºC from GUA ionic liquid at: a) 50, b) 25, c) 10, d) -10, e) -25 and f) -50 μA cm^{-2}. Nickel electrode.

Figure 4.- For the 0.9:1, Al(OH)$_3$: GUA molar ratio solution at 100ºC: A) Voltammetric curves at 10 mVs^{-1}. B) j-t transients recorded at different applied potentials: a) -0.50, b) -0.55 and c) -0.60 V. SEM images of deposits obtained at: C) 0.53 V and D) 0.58 V. Vitreous carbon electrode.

Figure 5.- Voltammetric curves at 10 mVs^{-1} recorded at 100ºC from: A) the 1.1:1, AlCl$_3$: PYR molar ratio solution at different reverse potentials, B) the 1:1, AlCl$_3$: IMI molar ratio solution, consecutive scans a) first, b) second scan. Vitreous carbon electrode.

Figure 6.- A) j-t transients recorded for 1:1 AlCl$_3$: IMI molar ratio solution at different applied potentials: a) -0.50, b) -0.55 and c) -0.59 V. SEM images of deposits obtained from 1.1:1 AlCl$_3$: PYR molar ratio solution at: B) -0.35, C) -0.40 and D) 0.50 V. Temperature 100ºC and vitreous carbon electrode. Q = -50mC.

Figure 7.- A) Voltammetric curve recorded at 10 mVs^{-1} from the 1.2:1, AlCl$_3$: GUA molar ratio solution, B) Voltammetric curves recorded at 10 mVs^{-1} from a) 1.3:1, b) 1.1:1 and c) 0.95:1 AlCl$_3$: GUA molar ratio solutions, C) Voltammetric curves recorded at 10 mVs^{-1} from 1.2:1 molar ratio solutions of: a) AlCl$_3$: GUA and b) AlCl$_3$: IMI, and D) j-t transients recorded for 1.2:1 AlCl$_3$: IMI molar ratio solution: a) -0.25 V and b) -0.37 V. Temperature 100ºC and nickel electrode.

Figure 8.- SEM images of deposits obtained potentiostaticaly at 100ºC from the 1.2:1, AlCl$_3$: IMI molar ratio solution at: A) -0.25 V and Q = -300 mC, B) -0.25 V and Q = -900 mC, and C) -0.37 V and Q = -500 mC. D) EDS analysis. Nickel electrode.

Figure 9.- From 1.2:1, AlCl$_3$: IMI molar ratio solution A) Chronopotentiograms at: a) 1.5, b) 2 and c) 2.5 mA cm^{-2}. SEM images of deposits obtained at: B) -1.5 mA cm^{-2} , Q = -500 mC, C) detail of B and D) -3 mA cm^{-2}, Q = -800 mC. Temperature 100ºC and nickel electrode.

Figure 10.- A) Voltammetric curves recorded at 10 mVs^{-1} from the 0.95:1, AlCl$_3$: GUA molar ratio solution, at temperature of: a) 100ºC, b) 110ºC and c) 120ºC. B) Chronopotentiograms

from the 1.30:1, $AlCl_3$: GUA molar ratio solution at 1 mA cm^{-2} at different temperatures: a) 130, b) 120 and c) 110 and d) 95ºC. Nickel electrode.

Figure 11.- SEM images of deposits obtained from the 0.95:1, $AlCl_3$: GUA molar ratio solution at 2 mA cm^{-2} at different temperatures: A) 100ºC, B) 110ºC C) 120ºC and D) 130ºC. Nickel electrode.

Figure 12.- SEM images of deposits obtained from the 1.3:1, $AlCl_3$: GUA molar ratio solution at 2 mA cm^{-2} at different temperatures: A) 95ºC, inset at higher magnification, B) 110ºC, inset at higher magnification. C) 110ºC at 1.5 mA cm^{-2} and D) -120ºC. Nickel electrode.

Figure 1
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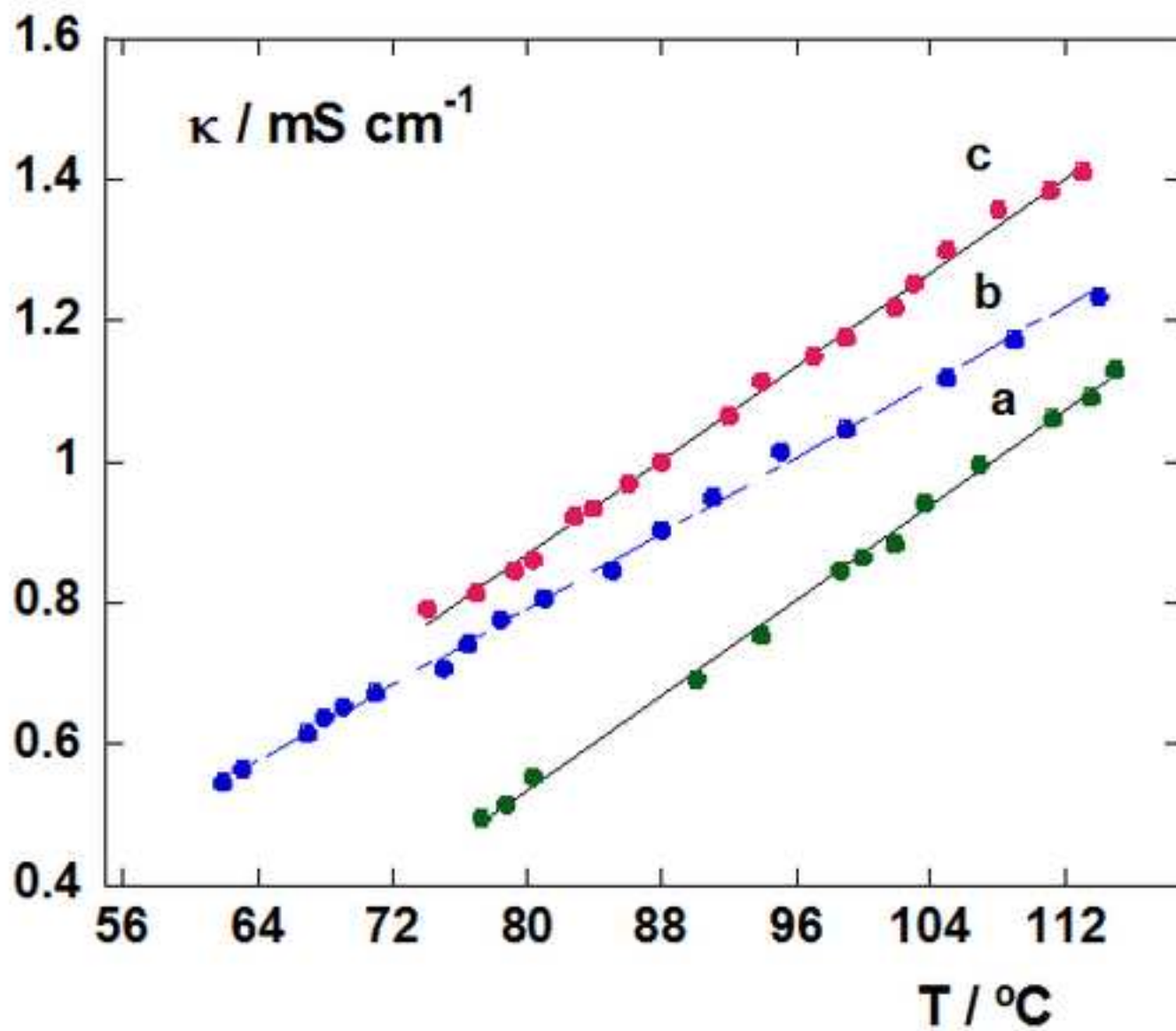
Figure 1

Figure 2
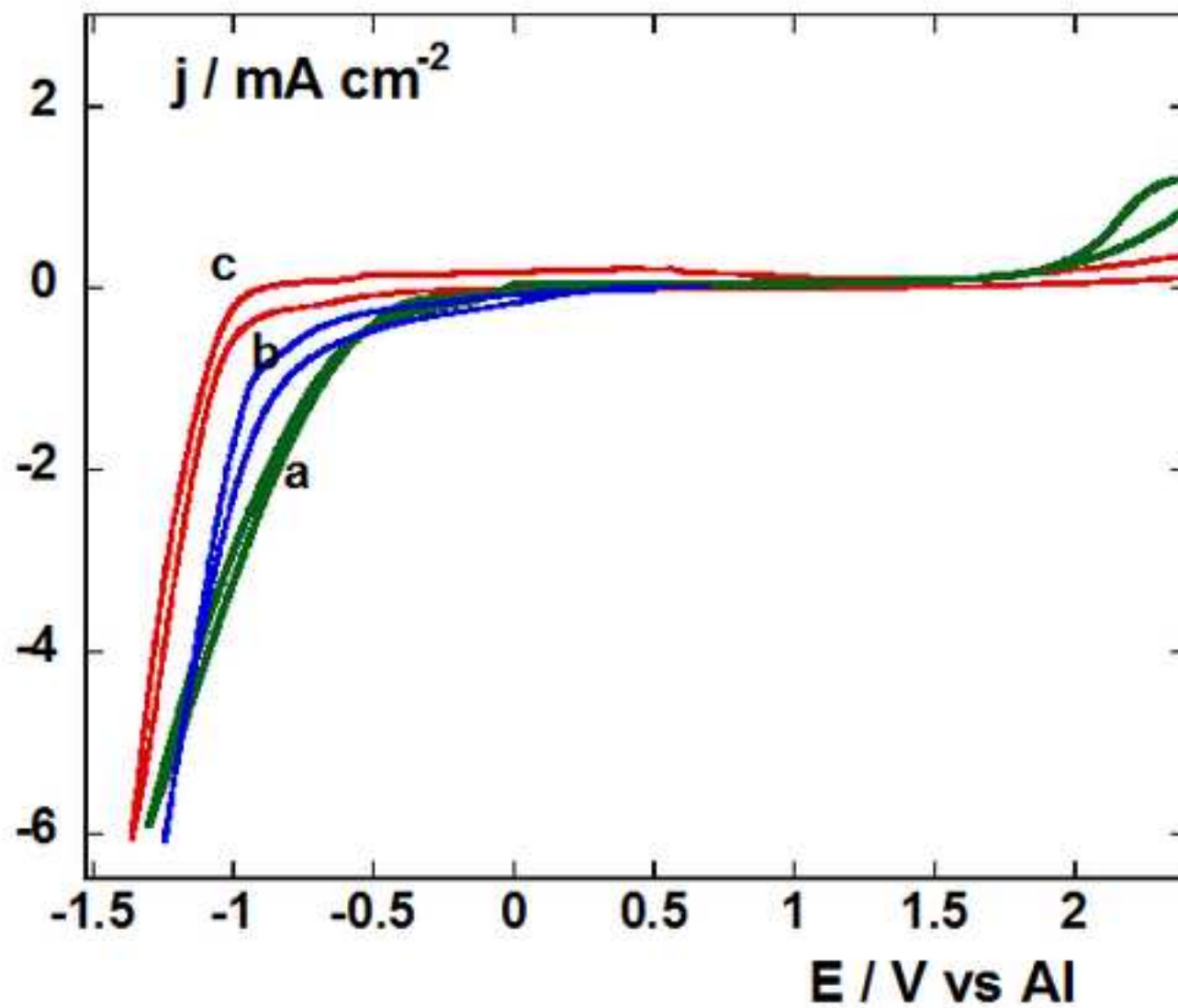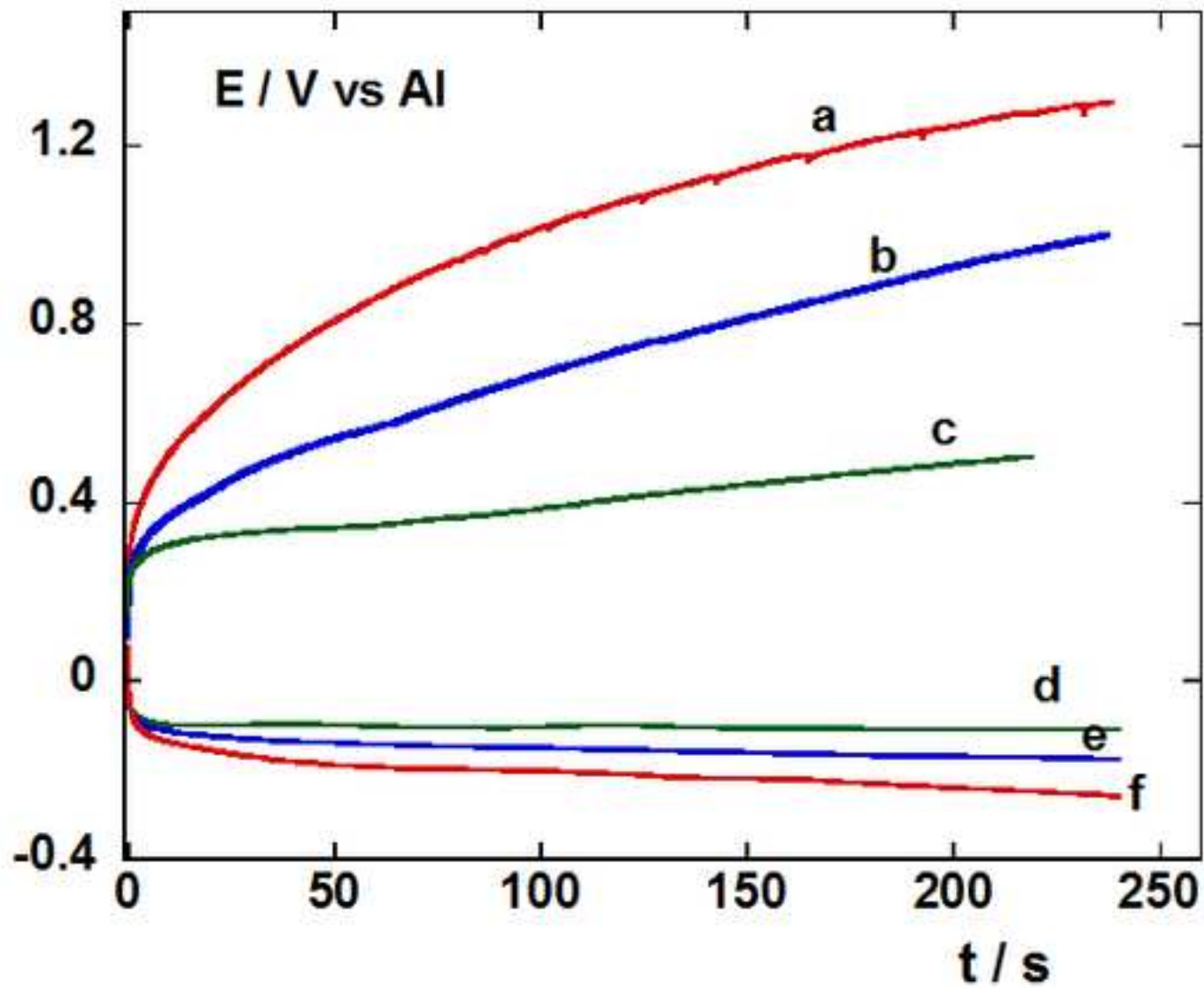
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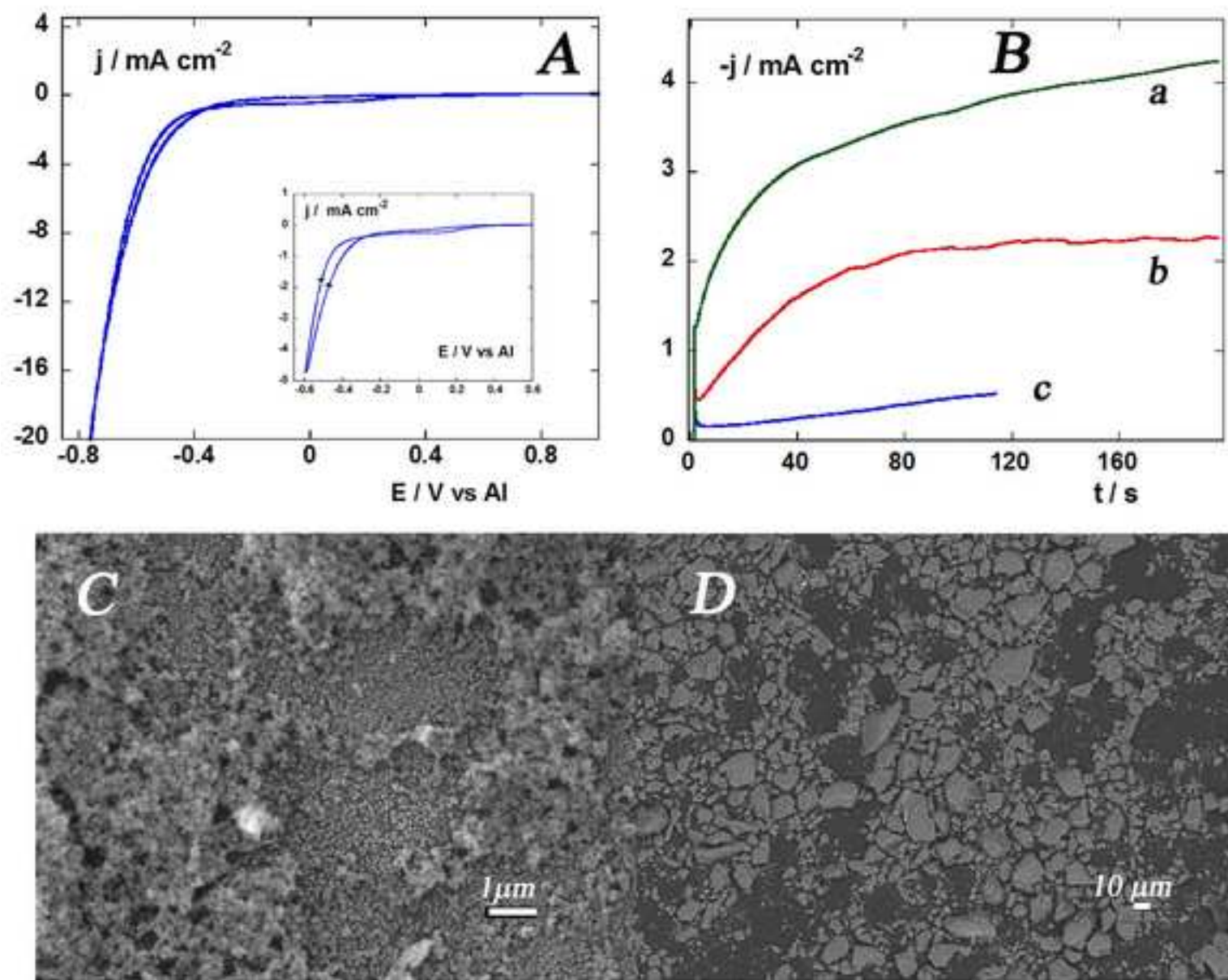
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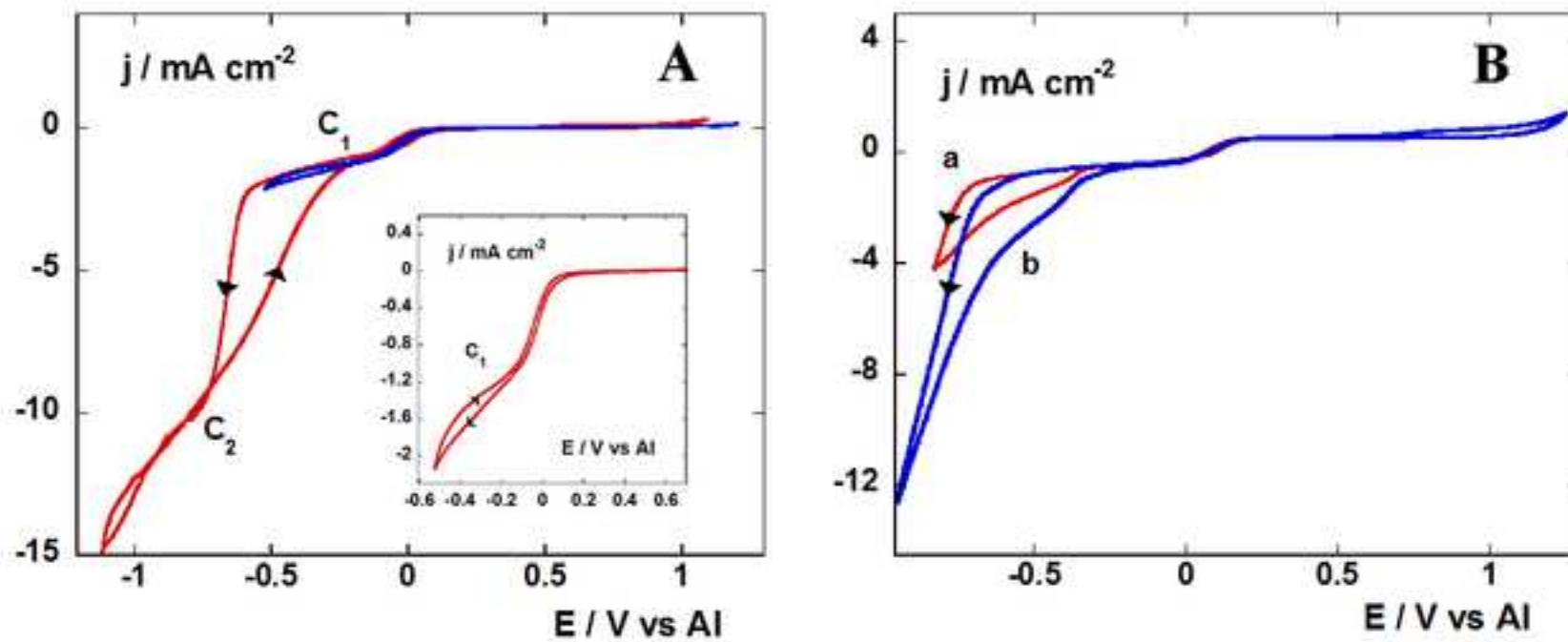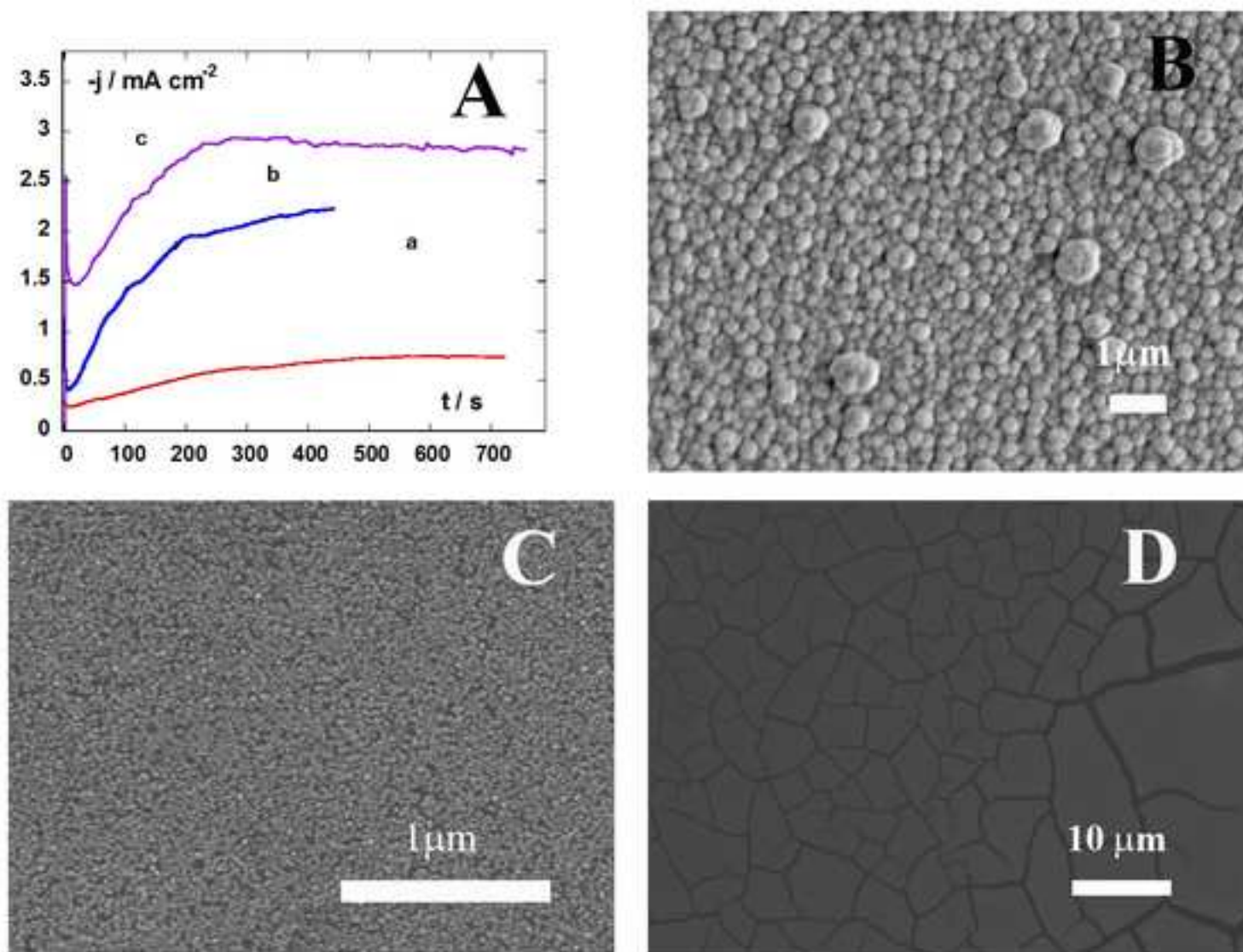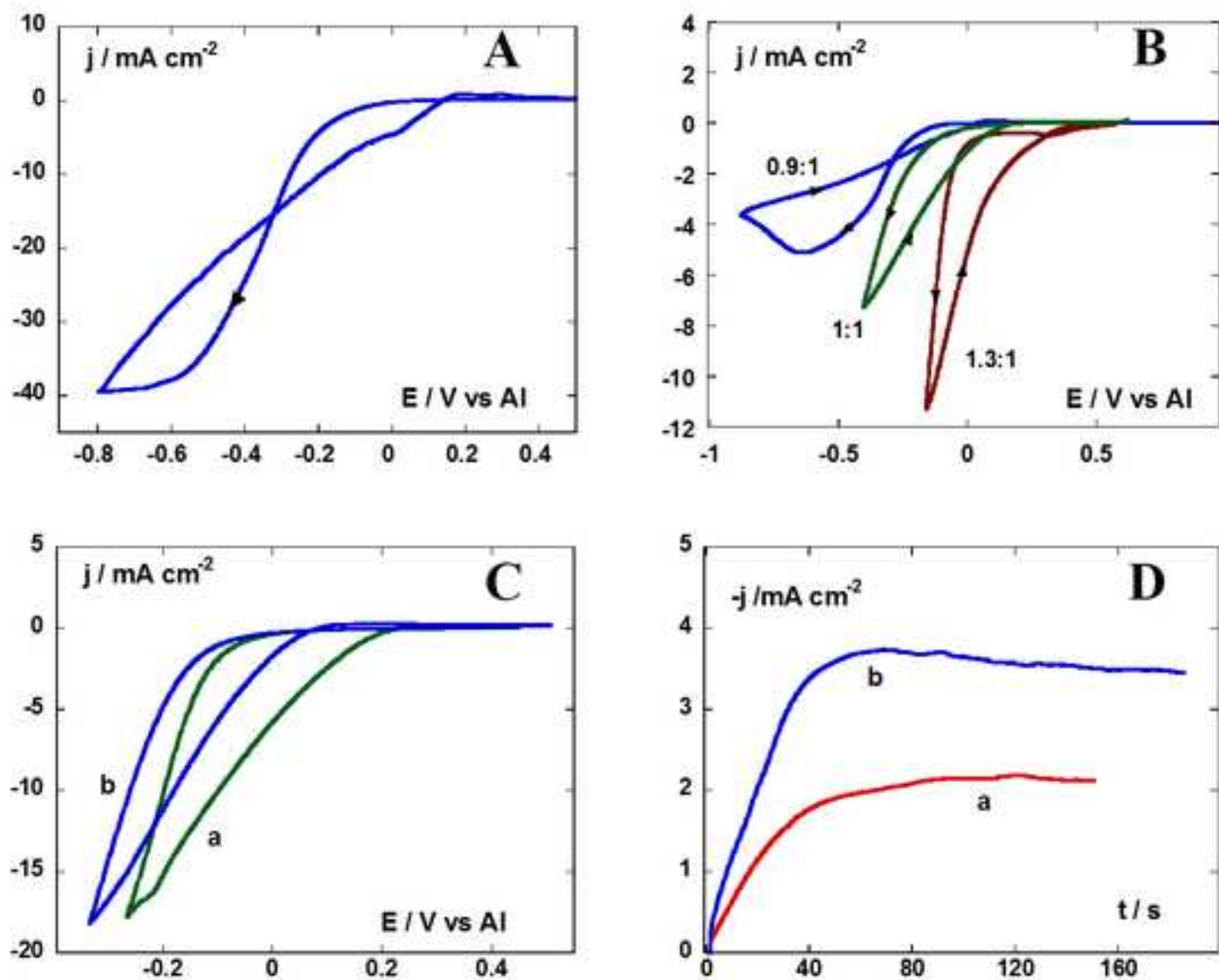
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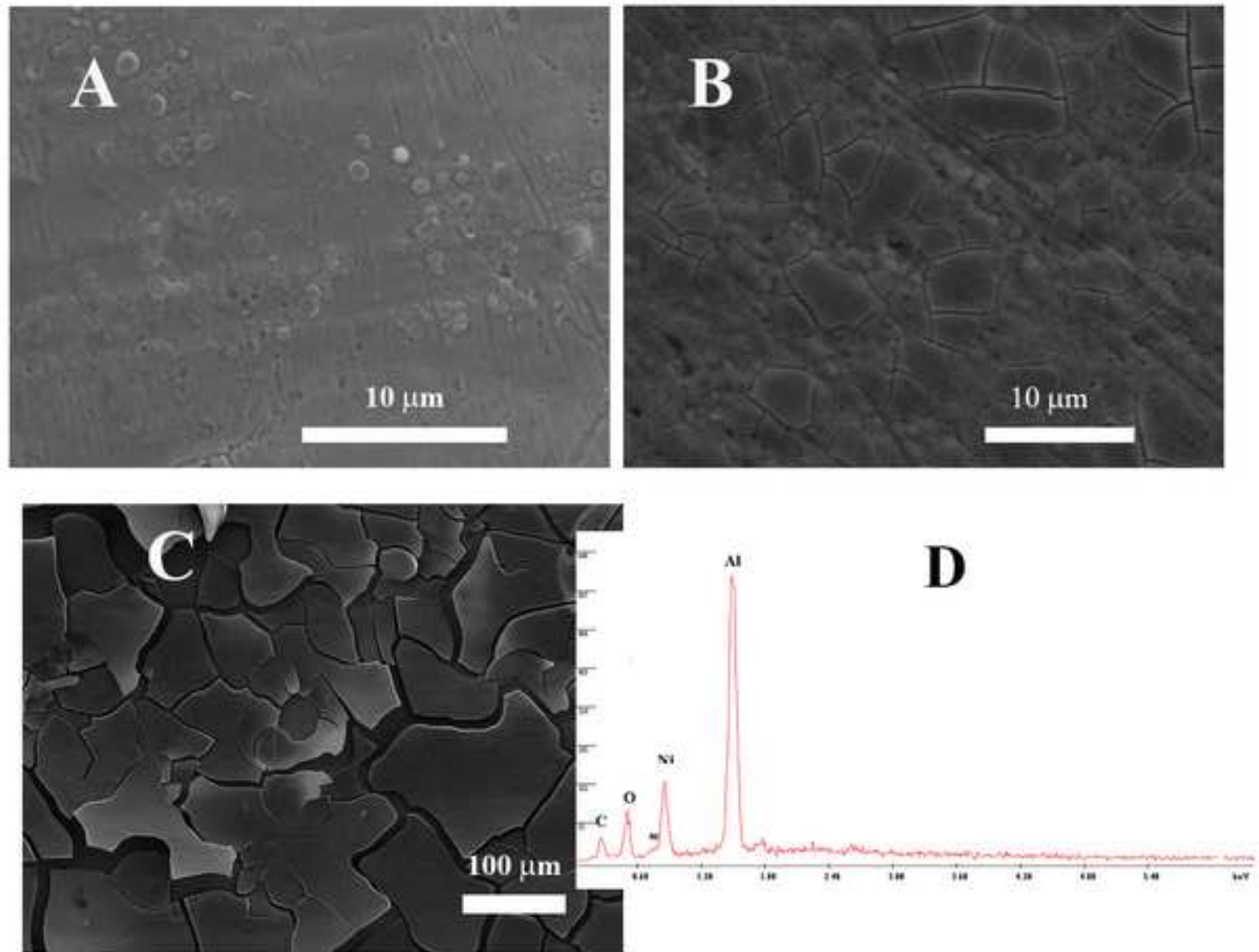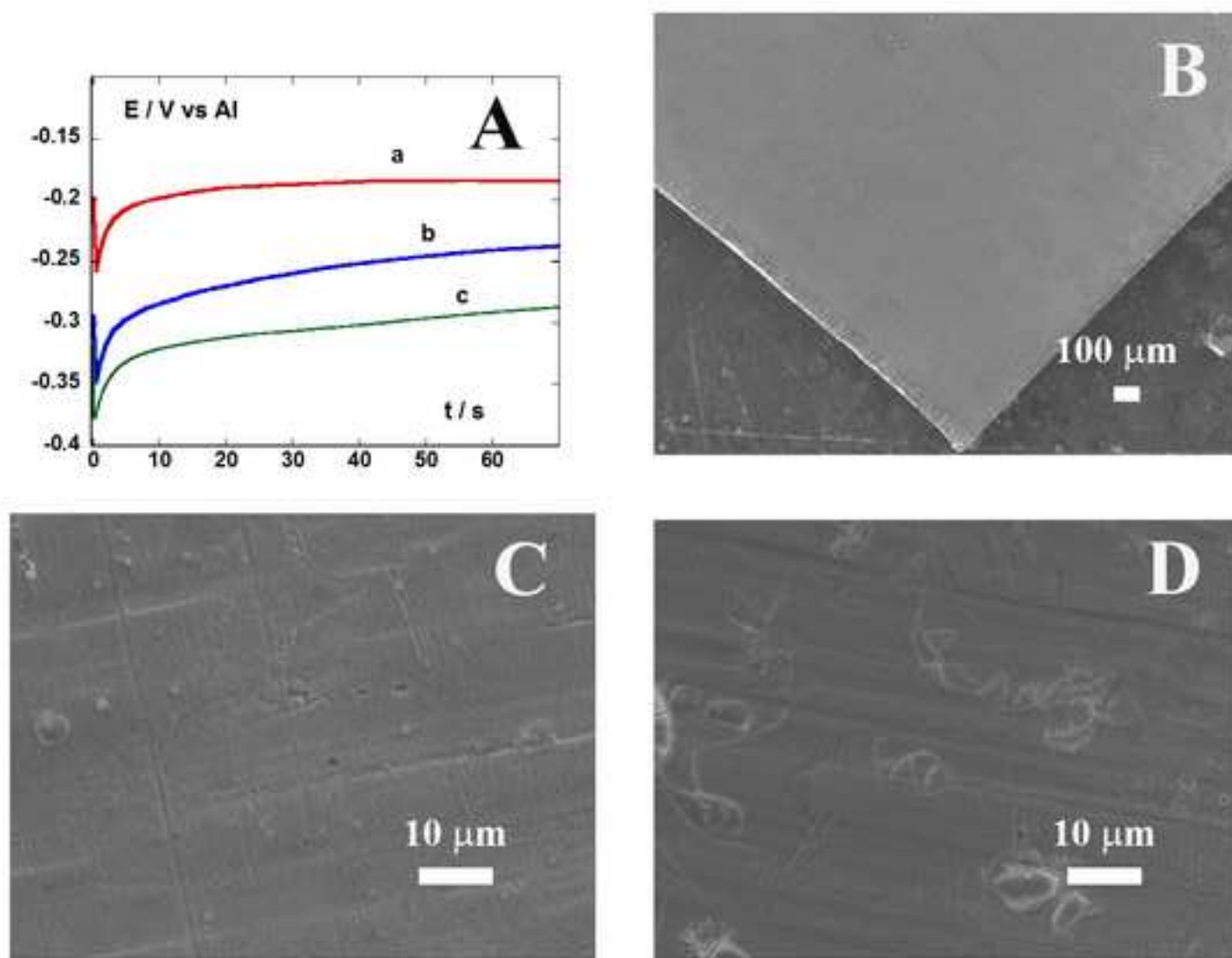**Figure 8**
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Figure 8

Figure 9
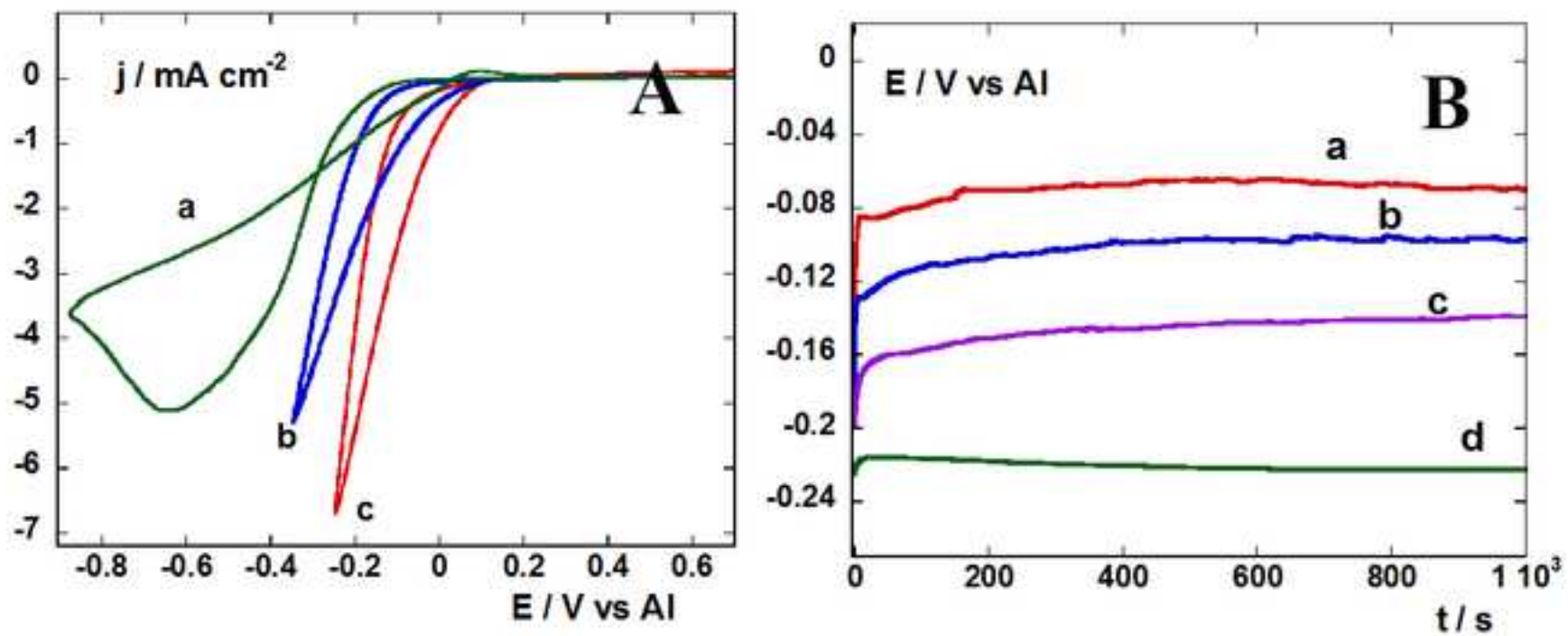**Click here to download high resolution image**

Figure 9

Figure 10
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Figure 10

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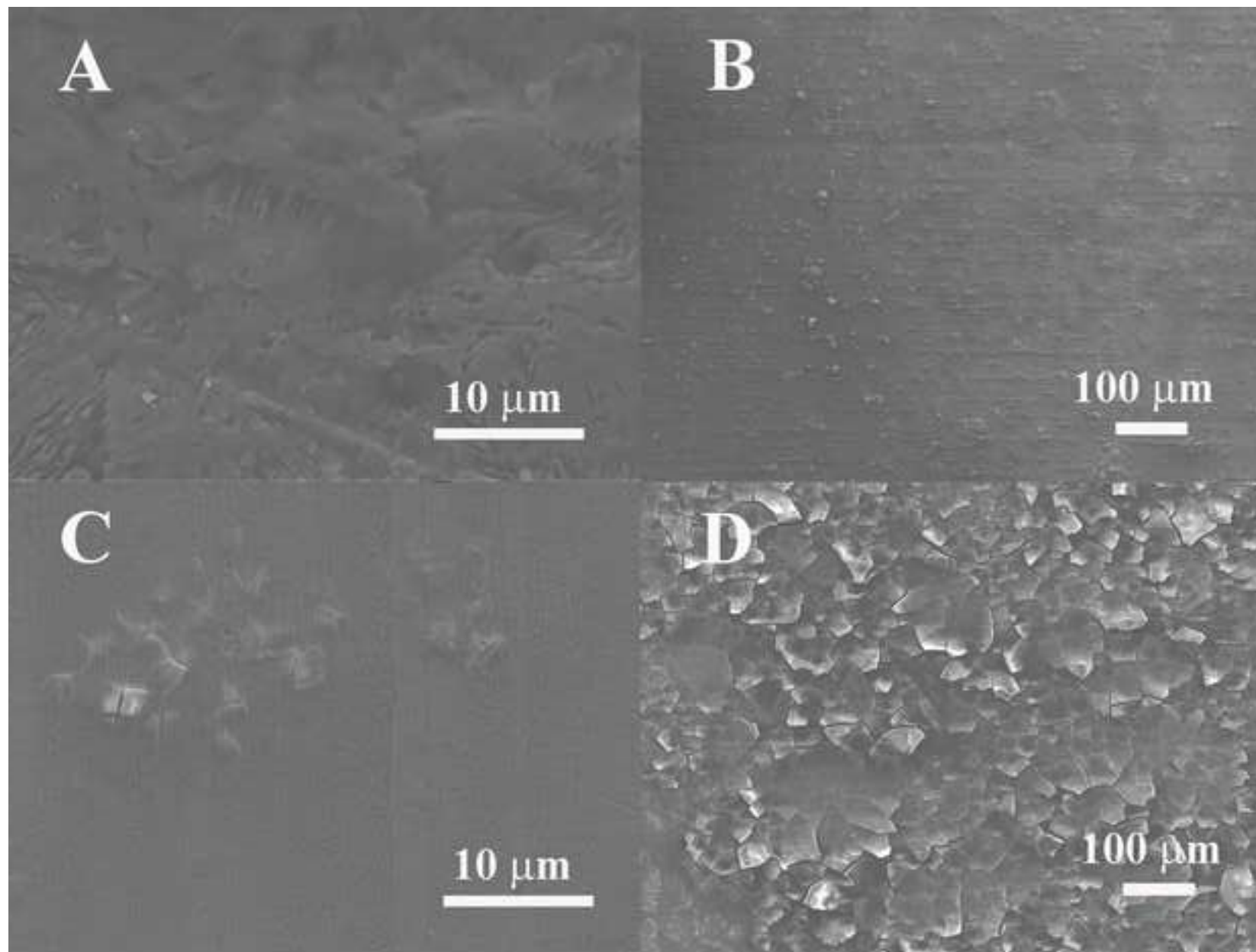**Click here to download high resolution image**

Figure 11

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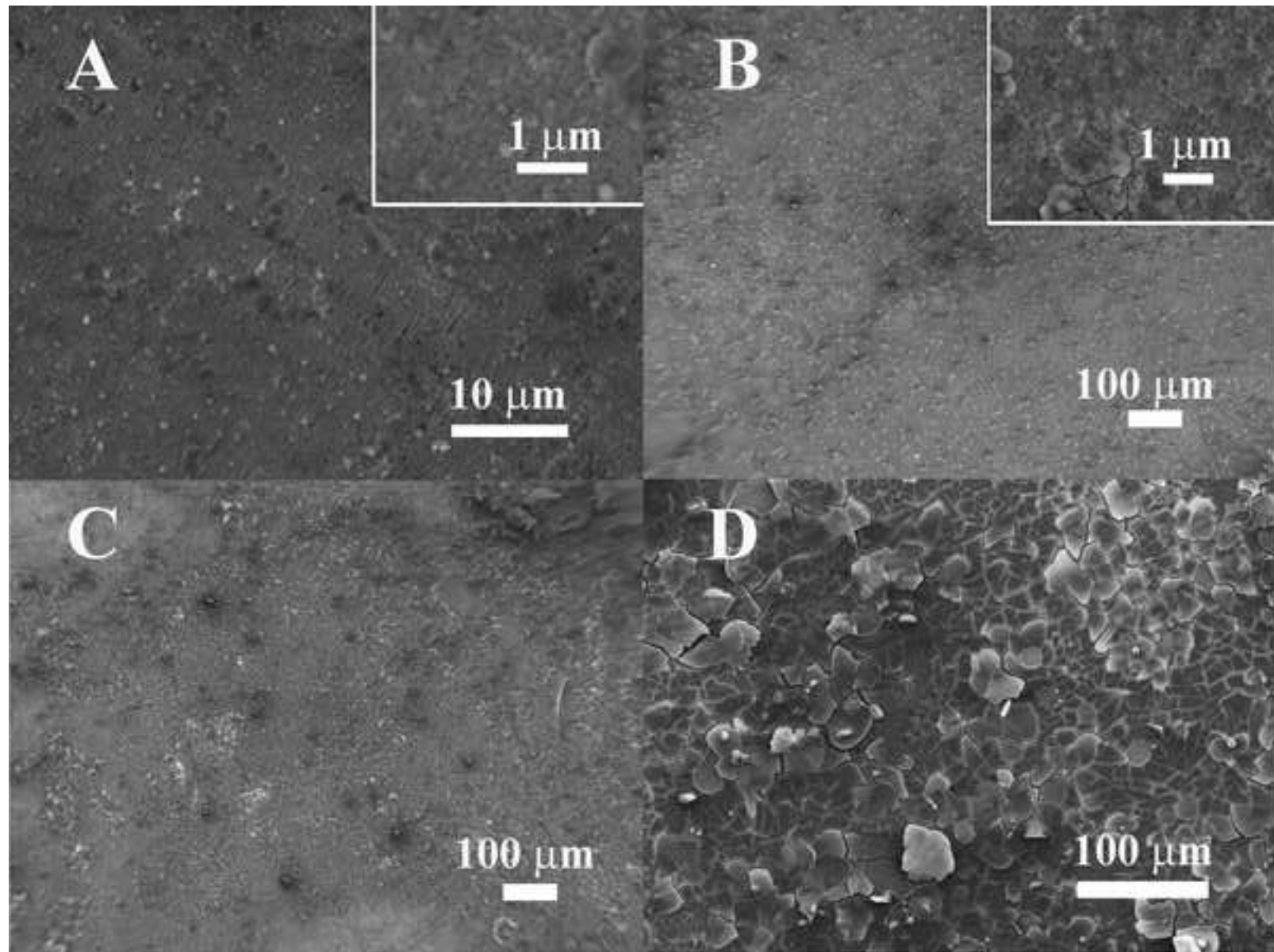**Click here to download high resolution image**

Figure 12

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