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Title: Aluminium electrodeposition from a novel hydrophobic ionic liquid tetramethyl guanidium -perfluoro-3-oxa-4,5 dichloro-pentan-sulphonate

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Abstract: Aluminium electrodeposition is demonstrated from a novel ionic liquid (IL), tetramethyl guanidinium -perfluoro-3-oxa-4,5 dichloro-pentan-sulphonate $[C_5H_{14}N_3^+][CF_2ClCFClOCF_2CF_2SO_3^-]$. This air and water stable ionic liquid owns a strong hydrophobic nature that was conceived to allow aluminium deposition in ambient conditions. This work presents the studies performed on the electrodeposition processes and reports images regarding the surface morphology of aluminium electrodeposited on vitreous carbon from solutions having a wide range of $AlCl_3$: IL molar ratios. The electrochemical window of this liquid is temperature dependent and sufficiently wide to allow aluminium deposition. The conductivity of solutions is highly influenced by the $AlCl_3$ content. Solutions that allow aluminium electrodeposition are characterized by an $AlCl_3$: IL molar ratio that ranges between 0.9 and 1.3. This compositional range probably represents the best compromise between $Al(III)$ concentration and conductivity values that allow sufficient mobility of the electroactive species. Nucleation and three dimensional growth was evidenced from both voltammetric and potentiostatic experiments. Cyclic voltammograms show a significant loop and $j-t$ transients the characteristic maximum, conventionally attributed to nucleation. Electrochemical evidences are confirmed by SEM images of the deposits, in which rounded or faceted crystals were observed depending on the electrodeposition conditions.

Reviewers' comments:

Reviewer #1: This manuscript reports interesting results about the electrodeposition of aluminium using tetramethyl guanidium -perfluoro - 3 - oxa- 4,5 dichloro-pentan-sulphonate, a novel hydrophobic ionic liquid, which is synthesized and supplied by Solvay Specialty Polymers. The effect of temperature, aluminium and bis-trifluoromethanesulfonimide lithium salt concentration, in the conductivity and electrochemical behavior of the electrolyte is evaluated and clearly discussed. However, the manuscript needs some improvements before acceptance for publication. My detailed comments are as follows:

At first the authors want to acknowledge the reviewer for the fruitful comment and then we tried to answer the questions

1. Introduction section (Page 3), the phrase "Electrodeposition could be a viable alternative due to the possibility to operate at moderate temperature (<100°C) and atmospheric pressure", seems to give the idea that the electrodeposition has not been used in the electrochemical deposition of aluminium at these conditions. Some works, such as G. Pulletikurthi et al. (Prog Nat Sci, 25 603-611 (2015)) and A. Bakkar et al. (Ref. 23 in the manuscript), that have used this process at room temperature should be cited in this part.

The objective of this paragraph was encourage the use of the electrodeposition for the preparation of deposits. At no time it was intended to give the impression that aluminum electrodeposition from IL was used for the first time. The paragraph has been rewritten and the suggested references included and consequently reordered.

2. Introduction section (Page 3), the phrase "Aluminium has a low reduction potential", is contrary to that reported in literature. In fact, because of the rather negative standard potential of Al, electrodeposition of Al from aqueous solutions is not possible due to hydrogen evolution at the cathode (Ref. 12 in the manuscript).

The words "low reduction" was used as synonym of "very negative" potential. In the new version in order to avoid misunderstandings between potential and overpotential, the phrase contains "very negative standard potential".

3. Page 10, just before the last paragraph, the authors comment that the voltammograms of Fig. 4B show the onset of reduction current at higher potentials if the aluminium content is increased. I suggest changing "higher potentials" for "more positive potentials" to avoid confusions.

According to the suggestion and in order to clarify the text, in this paragraph and others the "higher/lower" comparative were substituted by "more positive/more negative" in order to avoid confusions.

4. Page 11, in the discussion of the voltammetric curves obtained in the absence and presence of LiTFSI (Fig. 7), the authors comment that LiTFSI favours the aluminium deposition process, only based in the appearance of the reduction onset at

more positive potentials. This behavior could be associated merely at the improvement of the conductivity of the electrolyte,

The term favored, which in the new version has been removed, was referred to the increase in the conductivity of the solution due to the presence of LiTFSI. In none of the conditions, it was proposed that the presence of LiTFSI facilitates deposition process as additive or similar. The paragraph was rewritten in order to clarify the text.

since a favoring in the aluminium electrodeposition seems to be related at the formation of a broad peak between 0.4 V and 0 V vs. Al in the voltammograms, being more evident for the curve b of the Fig. 5. Note that this broad peak is not detected in the curve a of the Fig. 2, which was obtained for the blank solution at the same temperature that the curve b of Fig. 5. For this reason, I recommend to the authors consider this broad peak in the results discussion and insert a zoom in the figures of the zone where this peak appears, mainly for Figs. 2A, 4A, 4B and Fig. 7.

The broad band has been analyzed by the authors, but the fact that the scan reversal in this zone does not lead current loop and the appearance of the band at positive potentials respect to Al reference electrode would suggest a complex process. At this moment we present the description without the risk of possible wrong interpretation. The study of the first stages will be considered in near future on different kind of substrates in order to confirm their importance in the deposition process. Thank you for the suggestion.

5. *Page 12, at the beginning of the last paragraph, in the phrase "Considering most concentrated solutions and high temperature and small negative potentials", change "small" for "less".*

Thanks for the correction.

6. *Caption of Fig. 8, check value of b) in this part: "B) from 1.5:1, AlCl₃ : IL molar ratio solution at 125°C and applied potential: a) -0.1, b) 0.2, c) -0.3".*

The mistake was removed, thank you.

7. *I propose to the authors include the EDS analysis in the manuscript, at least the obtained for the sample of the Fig. 9.*

The EDS analysis has been included in the SEM figure.

At first the authors want to acknowledge the reviewer for the fruitful comment and then we tried to answer the questions

Reviewer #2: The article is interesting, but can be improved in the last part. English should be controlled.

We hope that English language has been improved

Page 6, from "Glassy carbon from Metrohm..." : Regarding alumina powder, 3.75 and 1.87 microns are strange dimensional values for an industrial product. Where did these values come from?

The supplier of alumina has been included in the experimental section. Alumina powder of different grade is usually used for the polishing of vitreous carbon.

Regarding the Deposition section (second half of page 13): The topic of this article is the achievement of Al deposits using this particular ionic liquid, but the section in which you actually focus on electrodeposition tests appears a bit short compared to the quantity of data shown about the preliminary electrochemical studies on different IL mixtures.

This manuscript is devoted to analyze the feasibility of aluminum electrodeposition using the proposed new ionic liquid. The conductivity data of different AlCl_3 :IL ratios were considered necessary in order to check the behavior of this physicochemical property when increasing the AlCl_3 content. Results relative to the effect of AlCl_3 concentration in the IL and to the variation of temperature were especially interesting. Although not included in the manuscript, voltammetric experiments were performed using all the prepared solutions, but it was considered that the incorporation of data with similar information does not contribute to new knowledge. However, in this revised version, more detailed comments have been included related to electrochemical responses. A new figure was also included.

For example, in the conclusion chapter you affirm that "our proposal using the presented liquid is to delimit/restrict the molar ratio of the AlCl_3 : IL solution between 0.9-1.3:1, molar ratio, so that adequate deposits can be obtained avoiding the use of extreme temperatures.", but no effective data on deposition near these limits was reported to confirm this "adequateness". Also how do you define adequateness? You should uniform better the reported data in the last section.

The use of solutions with AlCl_3 :IL > 1.4:1, due to the observed high viscosity, was considered of little practical interest for the final implementation. This behavior, combined with the fact that the experiments conducted in these solutions at both "moderate" temperature and potential did not lead to Al deposition, led us to advise against their use.

From the experimental results, it is clear that increasing the Al(III) content the process, as is usual when no relevant conductivity changes occur, takes place at less negative potentials. For this reason, the SEM images of deposits shown in the figures are prepared from AlCl_3 :IL = 1.15-1.2:1 solutions.

For the less concentrated AlCl_3 solutions, $\text{AlCl}_3:\text{IL} < 0.9:1$ at 100°C , the experimental voltammetric results demonstrate (Fig. 4A curve a) that the process is delayed to negative potentials and the progress of current is significantly slower with respect to the more concentrated solutions. The low deposition rate, also observed in potentiostatic experiments, discouraged us to propose this concentration range as feasible to prepare deposits in the future.

In the new version we tried to extend the information that could justify this selection.

You haven't specified in the text that the galvanostatic deposition process is "charge-controlled". If you specify again the same working electrode, you should also recall the reference and the counter.

All experiments are performed using the same kind of electrodes. We hope that the new version of the experimental section is clearer.

Fig.10, A and B are related to deposits obtained using different IL: AlCl_3 ratios, different potential and different end charge, it could be helpful at least to uniform the magnification of the images to better compare the differences between the deposits; also it appears quite difficult to define a "faceted morphology" from image 10B; in fact the image appears out of focus.

The text related to these images was rewritten in order to remark the differences. On the other hand the image 10B has been improved.

Figure 2A, Figure 4 A and B, Figure 5: adding trend arrows to the anodic or cathodic branches of the graphs could ensure the reader a better understanding of the trends between the curves.

According to the referee's suggestions in all voltammetric curves trend arrows have been included.

*Some of the language and the phrase construction used seems incorrect and can be improved, please revise the text (especially the experimental section).
Ex. In Experimental, "Struer polishing cloths", not "Polishing Struers Cloths".*

We hope that the text has been improved

Aluminium electrodeposition from a novel hydrophobic ionic liquid tetramethyl guanidium -perfluoro-3-oxa-4,5 dichloro-pentan-sulphonate

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Abstract

Aluminium electrodeposition is demonstrated from a novel ionic liquid (IL), tetramethyl guanidinium -perfluoro-3-oxa-4,5 dichloro-pentan-sulphonate $[\text{C}_5\text{H}_{14}\text{N}_3^+][\text{CF}_2\text{ClCFClOCF}_2\text{CF}_2\text{SO}_3^-]$. This air and water stable ionic liquid owns a strong hydrophobic nature that was conceived to allow aluminium deposition in ambient conditions. This work presents the studies performed on the electrodeposition processes and reports images regarding the surface morphology of aluminium electrodeposited on vitreous carbon from solutions having a wide range of AlCl_3 : IL molar ratios. The electrochemical window of this liquid is temperature dependent and sufficiently wide to allow aluminium deposition. The conductivity of solutions is highly influenced by the AlCl_3 content. Solutions that allow aluminium electrodeposition are characterized by an AlCl_3 : IL molar ratio that ranges between 0.9 and 1.3. This compositional range probably represents the best compromise between Al(III) concentration and conductivity values that allow sufficient mobility of the electroactive species. Nucleation and three dimensional growth was evidenced from both voltammetric and potentiostatic experiments. Cyclic voltammograms show a significant loop and j-t transients the characteristic maximum, conventionally attributed to nucleation. Electrochemical evidences are confirmed by SEM images of the deposits, in which rounded or faceted crystals were observed depending on the electrodeposition conditions.

Keywords: hydrophobic ionic liquid, aluminium chloride, aluminium electrodeposition, nucleation

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1. Introduction

Aluminium deposition has attracted much interest in the last decades. Recently favoured by the limitations imposed to utilization of hexavalent chromium, aluminium is being considered a valid alternative for aesthetic and functional coatings on metallic, and potentially also on polymeric substrates. Advantages of aluminium include non-toxicity, low density and possibility of anodization to obtain aesthetic finish with good corrosion resistance [1–3]. Conventionally Al coatings are obtained either by low pressure vapour phase deposition, e.g. sputtering [4,5] and CVD [6,7], or by high temperature processing, e.g. thermal spraying [8,9] and hot dipping [10,11]. Electrodeposition is a viable alternative [12,13] due to the possibility to operate at moderate temperature (<100°C) and atmospheric pressure, thus allowing to coat a broader spectrum of substrates.

Aluminium has a very negative standard potential and therefore it cannot be deposited from aqueous solutions, for this reason Al coatings have been prepared from organic solvents or inorganic molten salts [14–16]. Both solutions suffer from limitations, the former because important safety concerns due to solvent volatility and flammability, the latter needs high operative temperatures and is highly corrosive for the plating equipment, thus increasing energy consumption and operational costs. Industrial examples, limited by the abovementioned concerns, include the SIGAL (Siemens-Galvano-Aluminium) and REAL (Room-temperature Electroplated Aluminium) processes, developed respectively by Siemens and Philips.

Ionic liquids, on the other hand, possess properties that result suitable for electrodeposition of aluminium, such as low vapour pressure and high boiling point, non-toxicity and broad electrochemical window [17–19]. Several generations of ionic liquids have been synthesized and studied, having different properties in terms of ionic conductivity, melting point, electrochemical window and hydrophobicity due to different anionic and cationic structures. For example, a system with a given anionic structure has higher conductivity if the cation is based on imidazolium while cations based on pyrrolidinium impart a broader electrochemical window to the IL.

Considering the electrodeposition of Al, the chloroaluminate ionic liquids, obtained by mixing AlCl_3 with organic chloride salts, are the most studied and can be considered the first generation of ILs. In particular, systems are based on alkyl imidazole seem to give the better results. 1-ethyl-3-ethylimidazolium ($[\text{EMIm}]^+$) and 1-butyl-3-methylimidazolium ($[\text{BMIm}]^+$) appear to have attracted more attention in the scientific community [20–23]. It is reported in several studies that Al can only be deposited in acidic ILs, i.e. when the molar ratio between AlCl_3 and IL is greater than one, since this condition implies the presence of Al_2Cl_7^- , which is believed to be the only electroactive specie that can be reduced to metallic Al [24].

The main limitation of ILs having Cl^- as anionic component is their sensitivity to water and air. Especially when mixed to AlCl_3 , they become highly hygroscopic and water absorption makes Al deposition impossible. Therefore, such liquids cannot be used in an open-air system and this prevents their industrial application for Al plating. To overcome this issue two alternative solutions have been proposed: protecting the moisture sensitive plating solution with a barrier layer or developing a new class of ionic liquids having stronger hydrophobic nature. In the first case the mixtures of ($[\text{EMIm}]\text{Cl}$ and AlCl_3 or urea and AlCl_3) are protected from environmental moisture by a floating layer of decane [13,25]. In frame of the second approach, a further generation of ILs has been obtained and studied, which has higher hydrophobicity due to particular anionic structures, such as tetrafluoroborate (BF_4^-), trifluoromethylsulfonate (CF_3SO_3^-), bis(trifluoromethylsulfonyl)-imide ($[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$) and tris(trifluoromethylsulfonyl)methide ($[(\text{CF}_3\text{SO}_2)_3\text{C}]^-$) [26–28]. Electrodeposition of Al has been proved mainly from ILs having the bis(trifluoromethylsulfonyl)-imide anion, associated to several cationic structures. To the best of our knowledge though, also this generation of air and water-stable ILs is susceptible to environmental moisture once mixed with AlCl_3 [29]. For this reason the dissolution needs to be performed and operated under controlled and dry atmosphere, in order to prevent degradation and allow Al electrodeposition.

Therefore stronger hydrophobic nature is believed to be necessary to allow utilization of ILs for Al electrodeposition in ambient conditions. A new generation of ionic liquids is being synthesized and studied in collaboration with the R&D centre of Solvay

Specialty Polymers. The expertise of Solvay in fluorinated products and organic synthesis is of crucial importance to obtain ionic liquids that are air and water-stable also after the addition of AlCl_3 . In this manuscript we present results regarding electrochemical studies performed on one of these ionic liquids. The aim of this fundamental study is to determine whether it will be possible to electrodeposit Al with this electrolyte in an open-air system. In this way a further step towards industrialization of Al plating will be performed.

Since it is known from the literature that the hydrophobicity of ILs is mainly determined by the anionic structure [29], efforts were focused on the synthesis of systems having conventional cations coupled with innovative anions. The structure studied and presented here is composed by perfluoro-3-oxa-4,5 dichloro-pentane-sulphonate $[\text{CF}_2\text{ClCFClOCF}_2\text{CF}_2\text{SO}_3^-]$ and tetramethyl guanidinium $[\text{C}_5\text{H}_{15}\text{N}_3^+]$. Cyclic voltammetry and conductivity measures were performed both on blank IL and some of its mixtures with AlCl_3 . Al deposition was performed in potentiostatic conditions and the deposit was characterized by scanning electron microscopy.

2. Experimental

The study of the behaviour of the novel ionic liquid $[\text{CF}_2\text{ClCFClOCF}_2\text{CF}_2\text{SO}_3^-]$ $[\text{C}_5\text{H}_{15}\text{N}_3^+]$ (defined as IL from now on), supplied by Solvay Specialty Polymers, was performed on a blank solution prepared by melting a weighted amount of IL using a silicone bath under stirring in inert atmosphere. The resulting system consisted in a single phase liquid. The IL shows a melting point of 71°C and is not soluble in water.

The electroactive solutions were prepared by dissolving the aluminium source, anhydrous aluminium chloride (AlCl_3) from Sigma Aldrich, without further purification in the IL. The preparation of the AlCl_3 -IL solutions was also done under inert atmosphere. At first, the weighed amount of ionic liquid was set under nitrogen (N_2) atmosphere in a Schlenk flask: air was removed by repeatedly (4 series) evacuating and filling the flask with N_2 . Melting was afterwards performed in a silicone bath. Once the IL was liquefied, a weighed amount of AlCl_3 was added to obtain the desired AlCl_3 : IL

molar ratio. It was important to add the aluminium chloride quickly due to its hygroscopic nature. Then, the nitrogen atmosphere in the Schlenk flask was restored with the above mentioned protocol. The flask was dipped in the silicone bath, under constant stirring, until the dissolution was complete. AlCl_3 dissolves well and homogeneously in the ionic liquid. Several solutions were prepared, having an AlCl_3 : IL molar ratio ranging between 0.8 : 1 and 1.75 : 1. For the more concentrated solutions, dissolution was time consuming and a substantial increase in the viscosity was observed. Even though the IL is colourless and the AlCl_3 is yellowish/white, distinctive colour variations were observed depending on the AlCl_3 :IL molar ratio in solution. The solutions with AlCl_3 : IL molar ratio lower than 1.3 showed honey colour but, increasing the aluminium content, the coloration turned to orange and to pale pink for the most concentrated. The solutions prepared with lower concentration than 0.7 : 1, AlCl_3 :IL molar ratio were not considered in this work, because they did not lead to satisfactory electrochemical results in the preliminary analyses. In some experiments bis-trifluoromethanesulfonimide lithium salt (LiTFSI) from Sigma Aldrich was added to the solutions.

Conductivity was measured at different temperatures using a Metrohm 644 conductometer with a 52-92 CrisonTM 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 electrochemical study was performed using a microcomputer-controlled potentiostat/galvanostat Autolab (with PGSTAT 12 equipment and GPES software) using a standard three-electrode cell setup.

A vitreous carbon (Metrohm) of 3.14 mm^2 was used as working electrode. This electrode was mechanically polished prior to each experiment using alumina powder from VWR Prolabo, of different particle size (3.75 and $1.87 \mu\text{m}$), on Struers polishing cloths until mirror-like finish was obtained. Afterwards it was cleaned ultrasonically in Millipore Milli Q water for two minutes, in order to remove the alumina contaminants. Aluminium and platinum wires were used as pseudo-reference and counter electrodes respectively. Aluminium was mechanically polished with Struers SiC 4000 paper and platinum was heated in a flame to incandescence for several minutes after immersion

in aqueous solution of nitric acid (1:1). In all experiments the electrodes were immersed in the solution after removing the possible water residues, related to the cleaning treatment. Electrodes were also heated with hot air before immersion, in order to avoid solidification of the solution on the bare electrode surface after immersion. This may indeed occur due to temperature difference between the environment and the solution. Electrochemical experiments were performed 4 minutes after immersion.

Voltammetric experiments were performed at low scan rate, 5 mV s^{-1} or 10 mV s^{-1} , in order to record accurate curves. Deposits were prepared by means **potentiostatic** technique. The signal was applied for the time required to reach the selected charge. After electrodeposition the working electrode was quickly removed from the solution and exhaustively washed at first in warm dichloromethane, then dichloromethane-acetone mixtures and finally acetone, in order to remove the solution residues. Accurate elimination of residues was achieved after several rinses.

A field emission scanning electron microscope (JSM-7100F Analytical Microscopy) was utilized to investigate the surface morphology of the deposited films and energy dispersive X-ray analysis was used to determine the elemental composition of the **surface by means EDS Genesis software.**

3. Results and discussion

3.1. Conductivity measurements

Electrical conductivity is one of the characteristic physicochemical properties of ionic liquids. In this study, prior to electrochemical experiments, conductivity measurements were conducted both for the blank solution and for a set of AlCl_3 -IL solutions.

Conductivity measurements were made in a wide temperature range in two ways, at first increasing temperature and afterwards reducing it. Each conductivity value was acquired only after temperature stabilization was attained. No significant hysteresis was observed. Specific conductivities κ (mS cm^{-1}) are shown in Figure 1.

As shown in curve a, conductivity of the ionic liquid increases as the temperature rises, related to the increase in the mobility of the ions. For all explored temperatures however, the conductivity of the neat IL was relatively low.

Afterwards, the conductivity of a number of solutions prepared with increasing AlCl_3 : IL molar ratios was investigated. It was confirmed that the conductivity of pure liquid was significantly affected by the addition of AlCl_3 . For all solutions, as observed for the blank IL, the conductivity increased with temperature. Comparing the values corresponding to different solutions at a given temperature, progressive conductivity rise was observed with the aluminium content up to 1.25:1, AlCl_3 : IL molar ratio (Fig. 1 curves b, c and d). However, further increase of the AlCl_3 content in the solution, caused the conductivity to decrease (Fig. 1 curve e). Pronounced low conductivity values were observed for the solution having 1.75 : 1, AlCl_3 : IL molar ratio, at temperatures below 100°C (Fig. 1 curve f). The solutions with molar ratios up to 1.5 : 1 show a viscous aspect that forces to increase the temperature to achieve fluency, this increase of viscosity seems to be responsible of the observed drop of conductivity values, especially, at the lowest temperatures for the most concentrated prepared solution.

Due to the relatively high melting temperature of this liquid it was considered to work for general experiments at temperatures around 100°C to have better values of conductivity. Only for the experiments using the more concentrated solutions higher temperatures were considered. This is possible because the liquid was verified, by DSC and TGA, to be chemically stable above 200°C although these extreme temperatures have not been reached in any experiment.

3.2. Electrochemical characterization

3.2.1 Blank solution

At first, in order to establish the electrochemical window of pure ionic liquid, voltammetric experiments were performed at different temperatures using vitreous carbon as working electrode (Fig. 2A). The potential was scanned at 5 mV s^{-1} with

forward cathodic polarization. Voltammetric results indicate that widening sufficiently the potential range, oxidation and reduction of the ions present in the system occur. Features related to both reduction and oxidation processes were observed previous to massive bulk processes associated both to positive and negative currents, so that the electrochemical window was around 1.2 V at 150°C (Fig. 2A, curve a). By comparing the curves recorded at different temperatures, it is evident that the initio of these oxidation/reduction processes is temperature dependent. Lower temperatures lead indeed to wider electrochemical windows and lower involved currents (Fig. 2A, curves b-d), being the electrochemical window 1.8 V at 85°C. This indicates that anion oxidation and cation reduction are favoured at higher temperature. Successive scans, performed maintaining **the potential** limits, did not reveal changes in the profile of voltammetric curves at any temperature.

In order to check the electrochemical stability of the ionic liquid in the potential range corresponding to the electrochemical window, some long-time potentiostatic experiments were performed. In none of the selected conditions changes in the aspect or colour were observed in the blank solution and no film was formed on the electrode.

As a complementary study, experiments under quiescent conditions were carried out in order to investigate the electrochemical response of the ionic liquid to constant current demand. Six current values were explored, three negative and three positive. In all conditions, the potential profile shows monotonic evolution to quasi-stationary values, the potential becoming more negative as the demanded current was more negative (Fig. 2B, curves a-c). A similar behaviour was observed under growing positive currents, the stationary potential was indeed increasingly positive (Fig. 2B, curves d-f). Conversely it is remarkable that for positive demanded currents the differences between the attained potential values were greater than those recorded for the negative ones. These results indicate that, for this ionic liquid, the process associated to cation reduction is relatively more favoured than the process corresponding to anion oxidation. The observed potential change, to allow the same absolute current flow, was higher when the oxidation process was involved.

3.2.2 Aluminium chloride solution

Voltammetric experiments were conducted in order to analyse the electrochemical aluminium deposition process. The voltammograms were always recorded with forward cathodic scan, which resulted in a current decrease in all conditions. Reversing the scan at the onset of current appearance, a typical current loop associated to the nucleation and growth process [30] was recorded (Fig. 3, curve a), although this feature was not so clear for the most diluted solutions at low temperature. In no condition clear oxidation current was detected at potentials previous to ionic liquid oxidation. Extending the scan in the negative branch a shoulder was recorded previous to massive ionic liquid reduction (Fig. 3, curve b). Moderate stirring of the solution led to a slight increase in the recorded current, but foam formation in the bath dissuaded working at these conditions.

Solutions with different AlCl_3 concentration were investigated, for all of them similar voltammetric profiles were recorded, although depending both on aluminium concentration and on temperature clear differences in the potential value at which the reduction current appearance takes place was found. Figure 4A shows three voltammetric curves recorded from the 1 : 1, AlCl_3 :IL molar ratio solution at different temperature, exhibiting that the reduction current appears at more positive potential as the temperature is increased. A similar behaviour was observed, independently on the AlCl_3 :IL molar ratio for all the solutions investigated. In all cases, when a reduction peak was present, an advancement of the onset of the reduction current was observed when rising the temperature. This makes evidence that high temperature favours the electrodeposition process.

On the other hand, the comparison of voltammetric results from experiments performed from different solutions at fixed temperature, shows that, an increase in the AlCl_3 :IL molar ratio favours the appearance of the reduction current. The voltammograms show the onset of reduction current at more positive potentials as the Al(III) content is increased in the solution. It is also evident from Fig. 4B that for the lower AlCl_3 :IL molar ratio, (0.8 : 1), the process is not very favoured. However, this sequential advancing of the start of current appearance, raising the the Al(III) content

in solution, was not maintained when the AlCl_3 :IL molar ratio was brought above 1.3 : 1. A further increase in the AlCl_3 concentration led to the opposite behaviour. It was indeed necessary to raise the working temperature in order to achieve the current values expected after the increase of AlCl_3 concentration (Fig. 5 curve a). This result agrees with the conductivity decrease observed when the molar ratio of AlCl_3 in the solution was increased (Fig.1 curve e). However, increasing the temperature to 150°C , the predictable current advancement was observed (Fig. 5 curves b).

From the most concentrated solution considered (1.75 : 1, AlCl_3 :IL molar ratio) the current appearance was delayed to very negative potentials and it was not possible, even at 150°C (Fig. 5 curve c) to achieve current values similar to the ones recorded at lower concentrations.

As an attempt to increase the conductivity of the solution, the addition of bis-trifluoromethanesulfonimide lithium salt (LiTFSI) to the AlCl_3 -IL system was considered and its effect on aluminium electrodeposition was studied. First of all, the influence of the addition of LiTFSI on the conductivity of the blank solution was measured. A moderate conductivity increase was observed both with temperature and salt content (Fig. 6). For the most concentrated LiTFSI solution prepared (1 : 0.21, IL:LiTFSI molar ratio) a substantial decrease of the melting temperature was observed, so that the solution was liquid at room temperature. But at room temperature the conductivity was measured to be 0.056 mS cm^{-1} , about twenty times lower than the value observed at 100°C on the free Al(III) solution.

The influence of LiTFSI on aluminium electrodeposition was tested adding to a previously prepared 1.1 : 1, AlCl_3 : IL molar ratio solution, the necessary weight of LiTFSI to attain 1.1 : 1 : 0.07, AlCl_3 :IL:LiTFSI molar ratio. LiTFSI solubilisation was quick. The effect of LiTFSI in solution was evaluated, as is usual in this work, by comparing the onset of the reduction current in the voltammetric curve recorded for the AlCl_3 -IL system with and without the lithium salt, keeping the other parameters constant. The comparison between the voltammetric curves in the absence (Fig. 7, curve a) and in the presence of LiTFSI (Fig. 7, curve b) shows that when LiTFSI is added, the reduction current appears a little in advance and the current increases with a greater slope,

indicating that the higher conductivity of the solution imparted by LiTFSI, favours the aluminium deposition process. Lengthening the scan to more negative potential in the voltammetric experiments, the solution containing LiTFSI showed an incipient shoulder (Fig. 7, curve c). As for the LiTFSI-free solutions, reversing the scan, no oxidation current was detected, in the backward scan, before IL oxidation.

After cooling the AlCl_3 -IL-LiTFSI solution, an unexpected phenomenon was observed, the system showed biphasic behaviour. Two clear phases were observed at room temperature, the upper phase was liquid and the lower one solid. This is different from the homogeneous solid aspect that was observed at room temperature for the AlCl_3 -IL solutions prepared without LiTFSI, in all molar ratios investigated. This anomalous behaviour was previously described by Zein El Abedin et al. [31] using a water and air stable ionic liquid based on the bis(trifluoromethylsulfonyl)imide as solvent, although the reason of this behaviour was not fully clarified.

Trying to take advantage of this result, the electrodeposition of aluminium was performed from the upper phase of the solution at room temperature. As expected, the current appearance was delayed to negative potentials being the involved current much lower than the one previously measured and, even enlarging the scan to very negative potentials, the nucleation loop associated to nucleation process did not appear. This biphasic behaviour disappears at higher temperatures, at which a single phase was observed. Anyway, due to both this anomalous behaviour and the moderate advantage observed in the deposition process when LiTFSI is present in the solution, the subsequent study of aluminium electrodeposition in the proposed liquid was performed using LiTFSI-free solutions.

The potentiostatic analyses of aluminium electrodeposition were performed from several solutions at different potentials and temperatures, in quiescent conditions. The experiments were conducted by applying a single step signal, stepping the potential from a value where no reaction took place, to those potentials sufficiently negative to initiate the aluminium deposition process. Figure 8A shows, for the 1:1, AlCl_3 : IL molar ratio solution at relative low temperature, the recorded current density as a function of time during the deposition process conducted at different applied potentials. In all

experiments, it is possible to notice that in the beginning the cathodic current decreases rapidly due to double layer charging and, after the deposition process is revealed, the current shows a monotonic increase, the recorded current being greater as the applied potential is more negative. For more concentrated solutions, low negative potentials were needed in order to detect current associated to the deposition process.

Considering the most concentrated solutions at high temperatures, the recorded j-t transients show a behaviour which is similar to the ones previously observed for metal electrodeposition: sharp current peak related to the double layer charge and subsequent current increase that at low overpotentials smoothly approaches to a quasi-stationary value (Fig. 8B curves a and b). Applying more negative potentials, the typical current maximum appears in the j-t transients, followed by a subsequent current decay (Fig. 8B curves c and d). These features are clearly associated to nucleation and three dimensional grain growth [32,33]. This current decay evidences that some mass control exists, but the fact that the current profiles do not overlap at long deposition times seems to indicate that no pure diffusion control is governing the deposition due to possible changes in the effective area of the electrode during deposition. This fact avoids the experimental curves adjustment in feasible manner to nucleation and 3D growth models.

Some chronoamperometric experiments under stirring demonstrate that the process was affected by mass transport. Figure 8C shows the sudden current increase observed in a 1.15:1, AlCl_3 : IL molar ratio solution at -0.5V, associated to the onset of stirring by argon flow after 60s of polarization under stationary conditions. This abrupt current growth was favoured by the significant overpotential at which the experiment was performed.

In order to confirm aluminium electrodeposition and visualize the deposits, samples were prepared on vitreous carbon under different potentiostatic conditions. The previous voltammetric experiments allowed selecting, in each case, the potential range at which the deposits could be prepared. After careful removal of the electrolytic solution residues by means successive rinsing steps using dichloromethane and

acetone, the deposits were characterized by scanning electron microscope (SEM) and by energy dispersive X-ray analysis (EDS) to explore morphology and composition respectively. Visually, the deposits appear to be well adhering to the vitreous carbon substrate. At the lowest overpotentials and low deposition charges, rounded grains randomly distributed on the surface were imaged (Fig. 9). Increasing the involved deposition charge, coherent deposits were observed, SEM imaging evidenced that they were composed by rounded grains that achieved coalescence (Fig. 10A). From slightly low concentration applying more negative potentials, the density of deposited nuclei increased and showed small size (Fig. 10B). In all imaged samples, the EDS analysis of the deposit surface shows a strong peak for aluminium, confirming aluminium presence, while no signals related to ionic liquid composition (F, Cl or S) were detected, showing that no incorporation of the liquid occurs in the deposited film.

Over time, the prepared solutions darken, but it was confirmed by NMR that the colour change was not due to decomposition of the electroactive AlCl_3 -IL species. The stability after preparation of the solutions was tested in time (one month).

Reproducibility in the electrochemical experiments was obtained: despite the significant colour difference between fresh- and aged-solution, the cyclic voltammograms recorded were remarkably similar, confirming that any undetected degradation product that may be present within the AlCl_3 -IL solution does not seem to hinder the aluminium electrodeposition. During the elapsed time between experiments, the system was maintained at room temperature.

4. Conclusions

We have presented the first results of the additive free electrodeposition of aluminium from AlCl_3 in the water and air stable perfluoro-3-oxa-4,5 dichloro-pentan-sulphonate-tetramethyl guanidinium $[\text{C}_5\text{H}_{15}\text{N}_3^+][\text{CF}_2\text{ClCFClOCF}_2\text{CF}_2\text{SO}_3^-]$ ionic liquid, from Solvay Specialty Polymers. The evidences of voltammetric nucleation loop, the current increase in the j-t transient and, definitively, the observation of deposit formation allow concluding that aluminium deposition occurs using AlCl_3 as a source of aluminium (III).

This ionic liquid solubilises well AlCl_3 salt up to an AlCl_3 :IL molar ratio of 1.3 : 1. It was possible to solubilise AlCl_3 at higher molar ratios, but an important increase in the apparent viscosity was observed that forced to increase the temperature during the preparation of the solution and during the electrochemical experiments. In all conditions, the prepared solutions show single phase behaviour.

For the solutions in which AlCl_3 : IL molar ratio was greater than 0.8, significant reduction current loop in the voltammetric curves was recorded reversing the scan at the onset of reduction current. At lower Al(III) concentrations the reduction current appearance occurs at very negative potentials and no clear current nucleation loop was recorded that discouraged to investigate aluminium deposits preparation at these conditions.

Aluminium deposition process was enhanced by both temperature and AlCl_3 : IL molar ratio increase. However, the subsequent increase of Al(III) concentration (>1.4:1, AlCl_3 : IL molar ratio) due to the associated lowering of conductivity exerts a detrimental effect in the overall electrodeposition process slowing deposition process forcing to rise the temperature. From this, in the future the possible working proposal with the most concentrated AlCl_3 -IL solutions is inadvisable.

For these reason, in order to optimize the results on different substrata, our proposal using the presented liquid is to restrict the molar ratio of the AlCl_3 : IL solution between 0.9-1.3:1, molar ratio, solutions which preparation is no-time consuming and their physicochemical properties are adequate as the manner the deposits can be obtained avoiding the use of extreme temperatures. The use of LiTFSI as possible enhancer of solution conductivity resulted not recommended using this ionic liquid due to the induced biphasic behaviour that makes in evidence that species with different behaviour coexist in the solution. This novel liquid constituted by the perfluoro-3-oxa-4,5 dichloro-pentan-sulphonate is advantageous since it does not show the biphasic behaviour observed in the aluminium solution containing its predecessor, the bis(trifluoromethylsulfonyl)imide, even though its melting temperature is higher.

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Captions for figures

Figure 1.- Conductivity values at different temperatures for: a) blank solution, b) 1:1, c) 1.1:1, d) 1.25:1, e) 1.5:1 and f) 1.75:1, AlCl_3 :IL molar ratios.

Figure 2.-From the blank solution: A) Voltammetric curves at 5mVs^{-1} recorded at different temperatures: a) 150, b) 125, c) 100 and d) 85°C , and B) Chronopotentiometric curves recorded at 105°C at: a) -35, b) -80, c) -159, d) 35, e) 80 and f) $159\ \mu\text{Acm}^{-2}$. Vitreous carbon electrode.

Figure 3.- Voltammetric curves at 5mVs^{-1} for the 1.2:1, AlCl_3 : IL molar ratio solution at 102°C . Different reverse potentials. Vitreous carbon electrode.

Figure 4.-Voltammetric curves at 5mV s^{-1} : A) from the 1:1, AlCl_3 : IL molar ratio solution at different temperatures: a) 75, b) 85 and c) 100°C , and B) at 100°C for different solutions: a) 0.8:1, b) 1:1 and c) 1.2:1, AlCl_3 : IL molar ratios. Vitreous carbon electrode.

Figure 5.-Voltammetric curves at 5mVs^{-1} for the 1.5:1, AlCl_3 : IL molar ratio solution at: a) 125°C , b) 150°C and c) for the 1.75:1, AlCl_3 :IL molar ratio solution at 150°C . Vitreous carbon electrode.

Figure 6.- Conductivity values at different temperatures for: a) blank solution, b) 1:0.07 and c) 1:0.21, IL : LiTFSI molar ratios.

Figure 7.- Voltammetric curves at 10mVs^{-1} at 110°C for: a) 1.1:1, AlCl_3 : IL molar ratio solution and for 1.1:1:0.07, AlCl_3 :IL : LiTFSI molar ratio solution at different negative limits: b) 0.25 and c) 0.43 V. Vitreous carbon electrode.

Figure 8.-j-t transients A) for 1:1 AlCl_3 : IL molar ratio solution at 85°C at different applied potentials: a) -0.25, b) -0.35 and c) -0.45 V, B) from 1.5:1, AlCl_3 : IL molar ratio solution at 125°C and applied potential: a) -0.1, b) -0.2, c) -0.3 and d) -0.38 V and C) for 1.15:1, AlCl_3 : IL molar ratio solution at 125°C applying -0.5 V, the first 60 s under quiescent conditions and the rest under stirring with argon flow. Vitreous carbon electrode.

Figure 9.- SEM images of deposit obtained at -0.15 V for the 1.2:1, AlCl_3 :IL molar ratio solution at 110°C. Inset the corresponding EDS analysis. Q = -5 mC.

Figure 10.- SEM images of deposits obtained at 110°C: A) for the 1.2:1, AlCl_3 : IL molar ratio solution at -0.2 V and Q = -50 mC, and B) from the 1.15:1, AlCl_3 : IL molar ratio solution at -0.3 V and Q = -40 mC.

Figure 1
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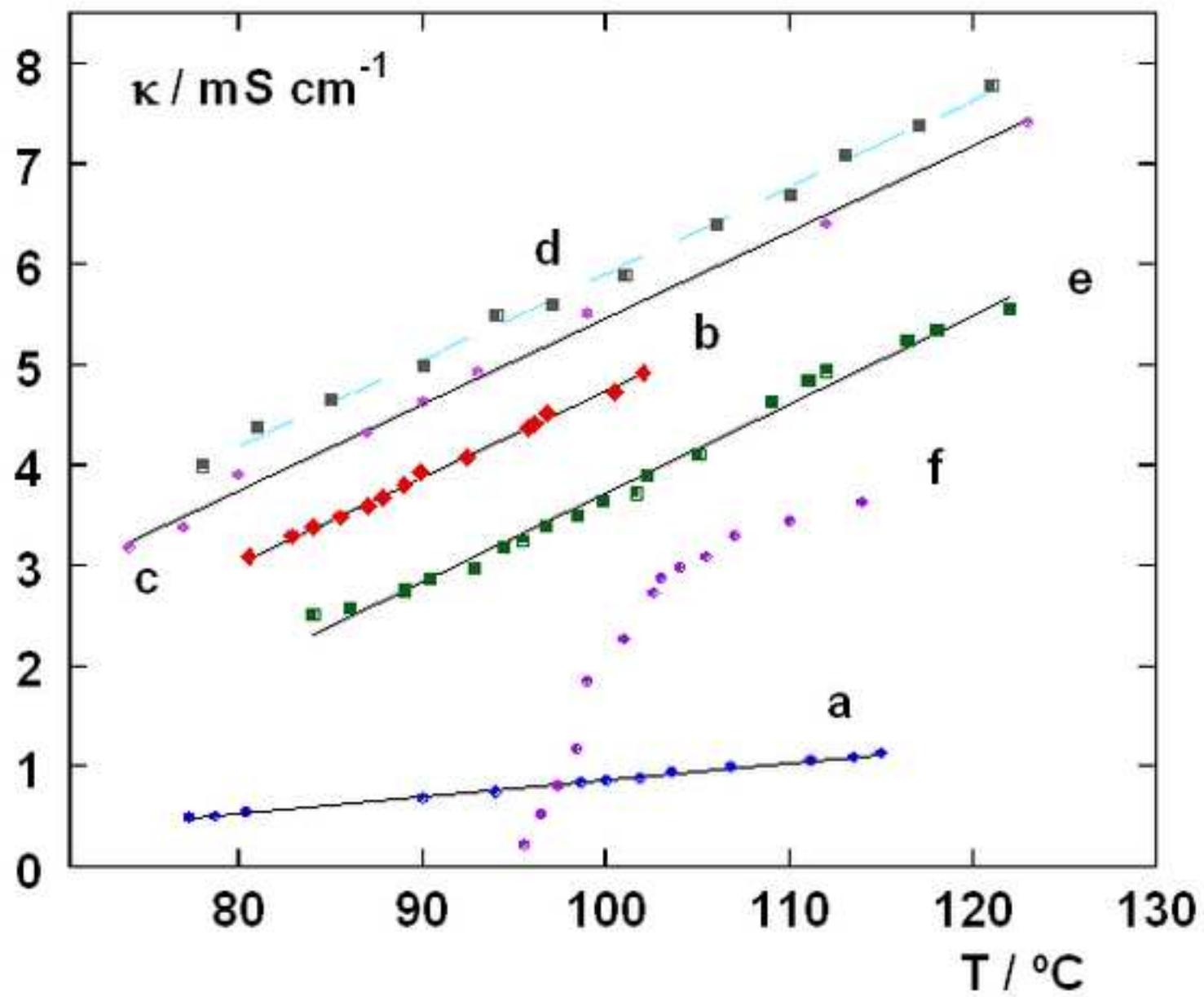


Figure 1

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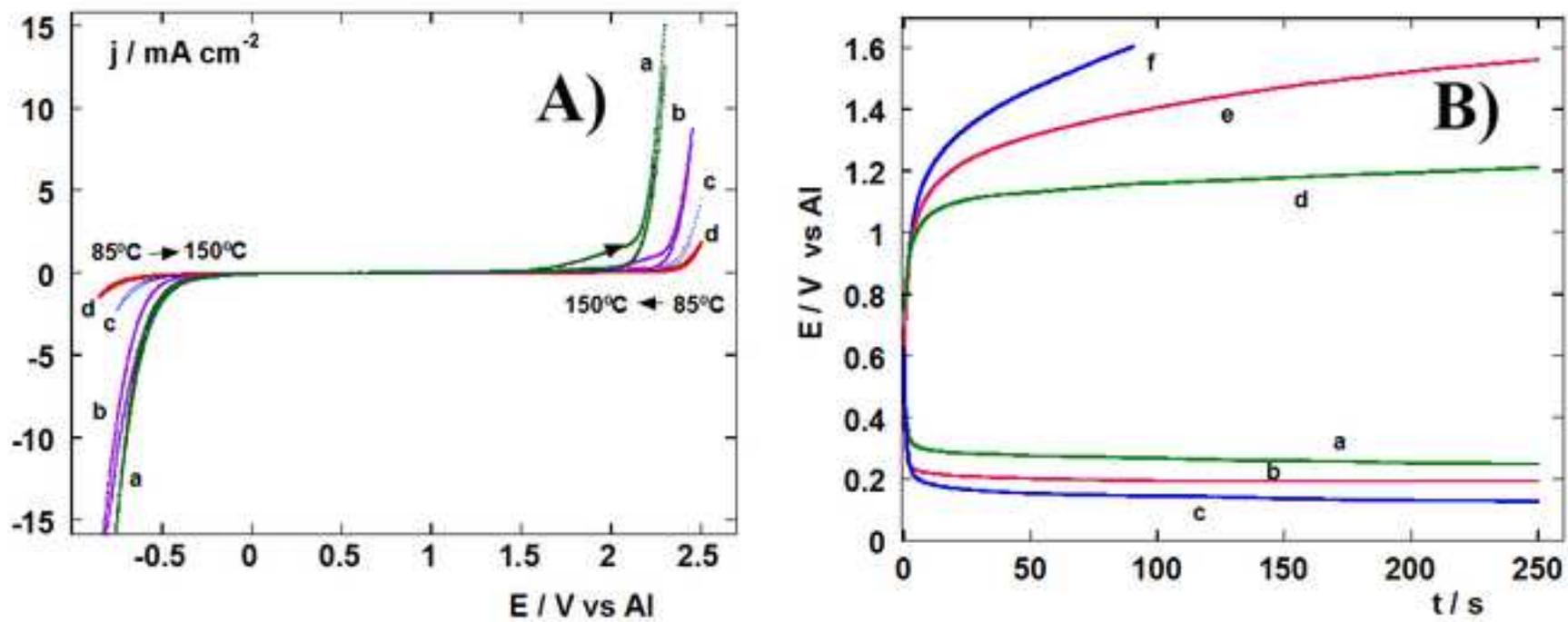


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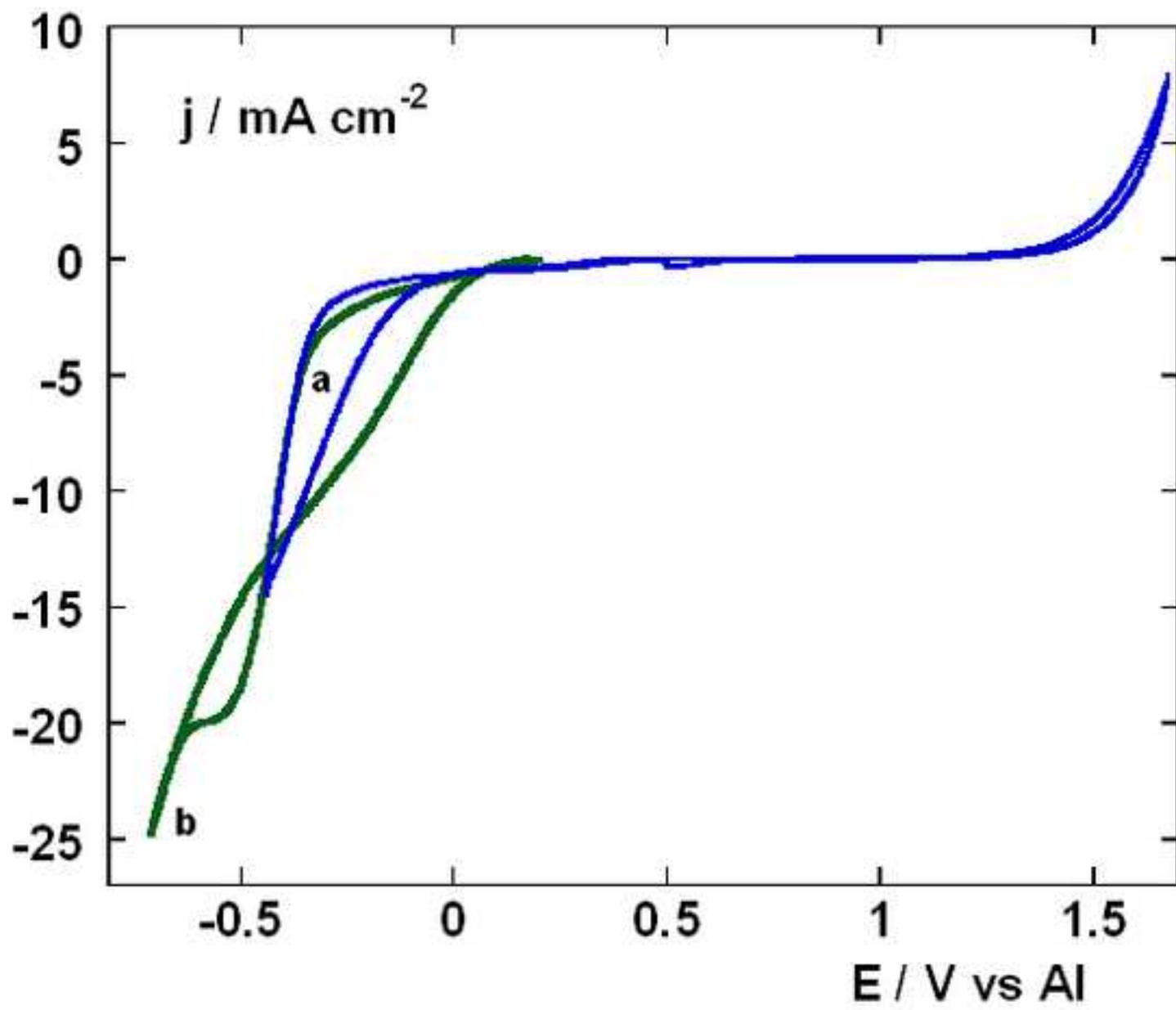


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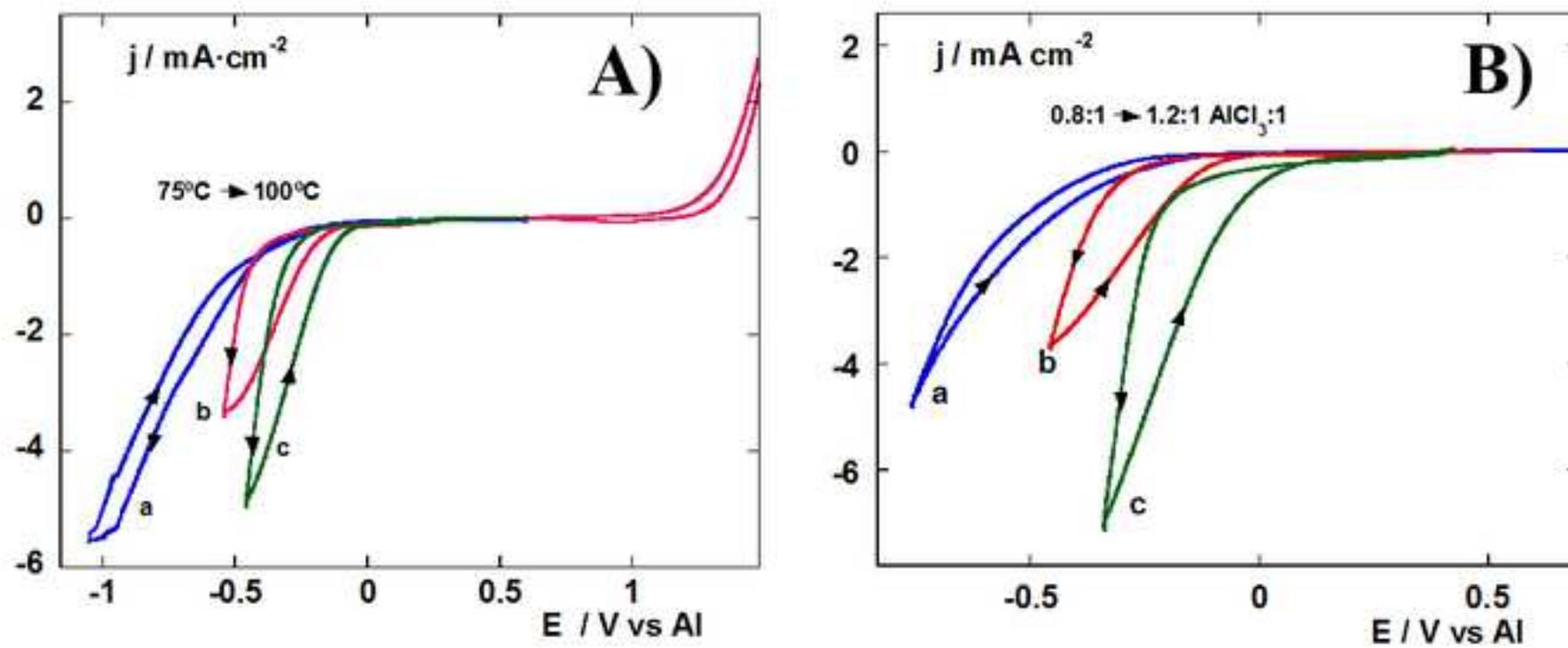


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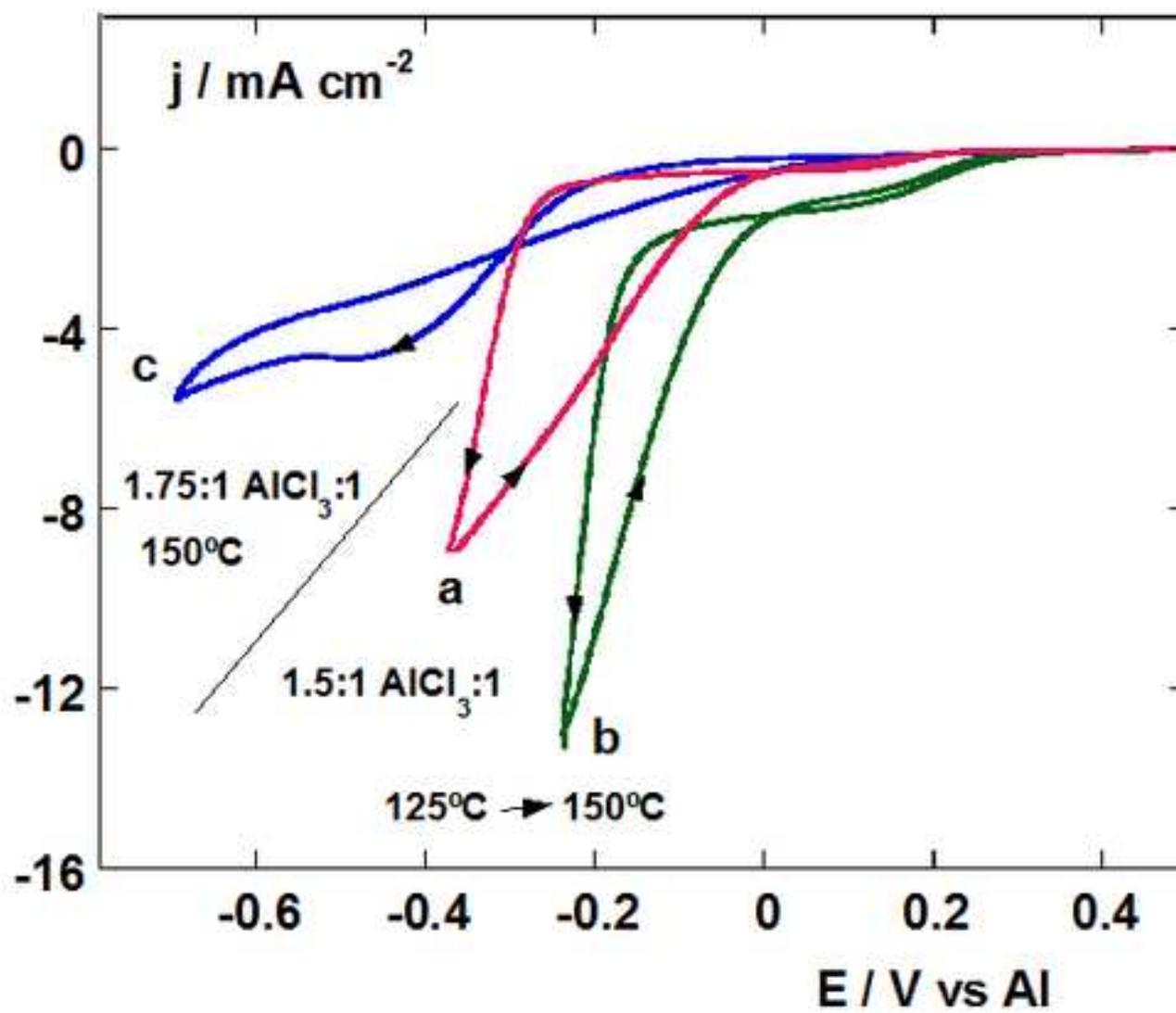


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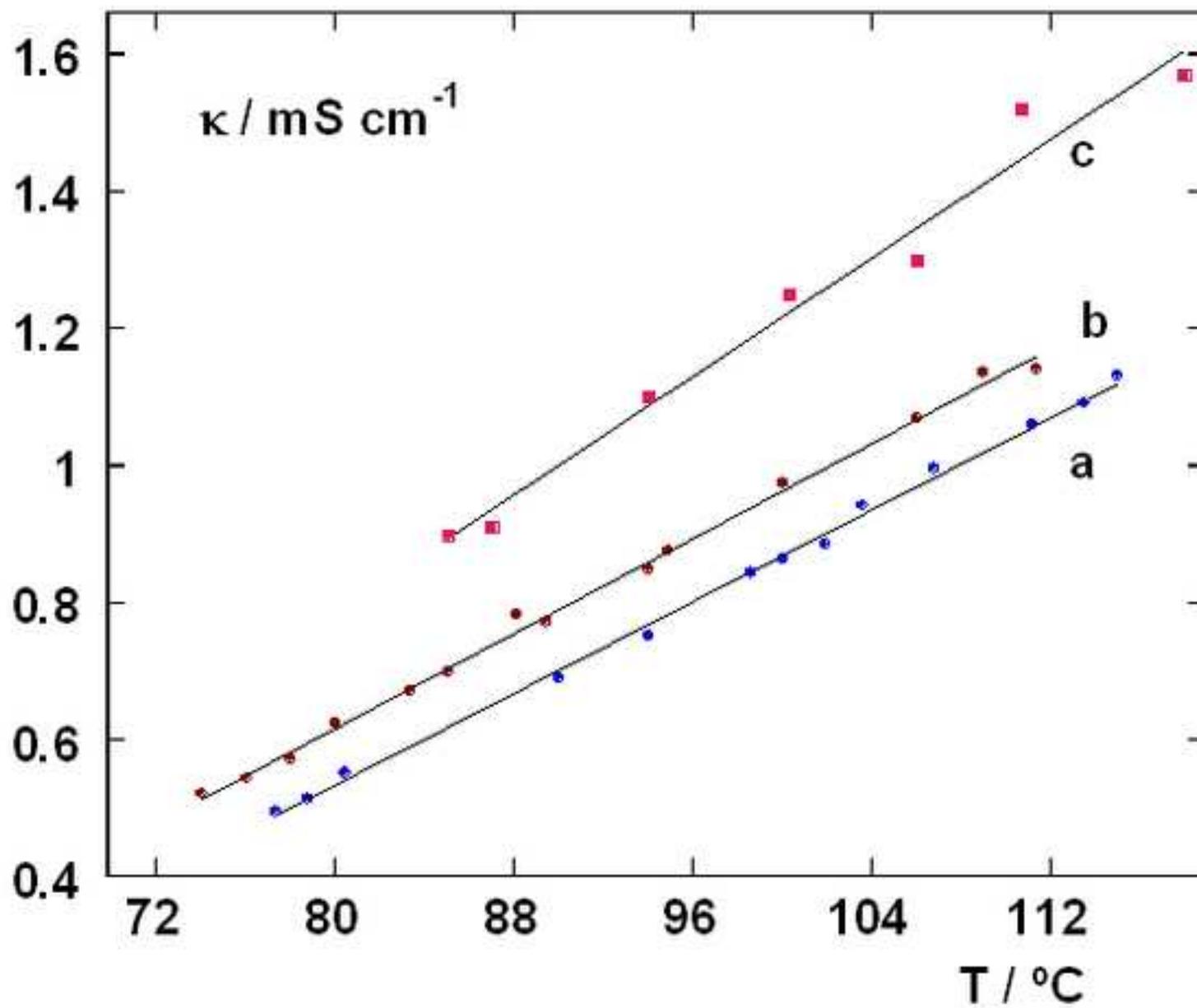


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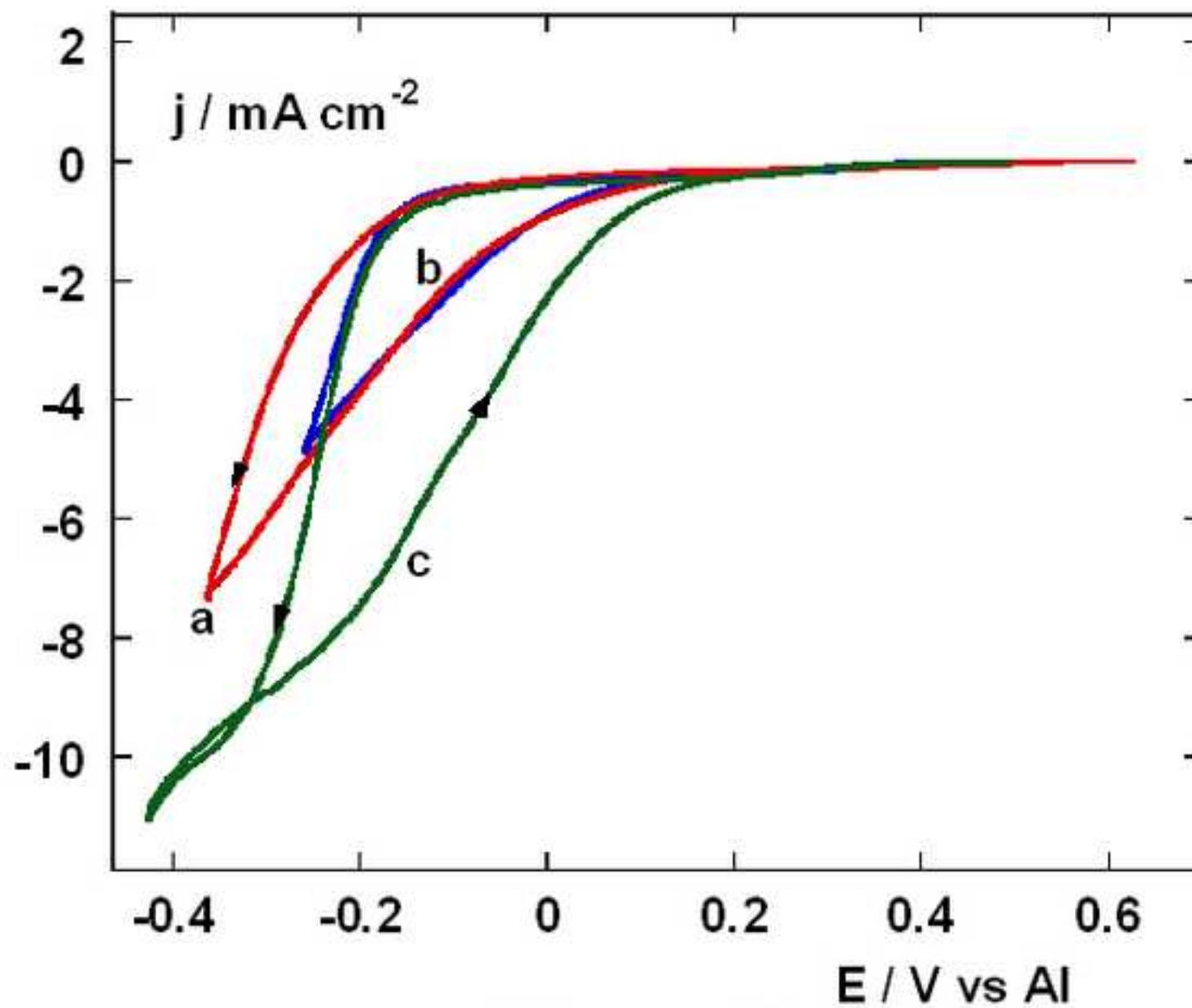


Figure 7

Figure 8
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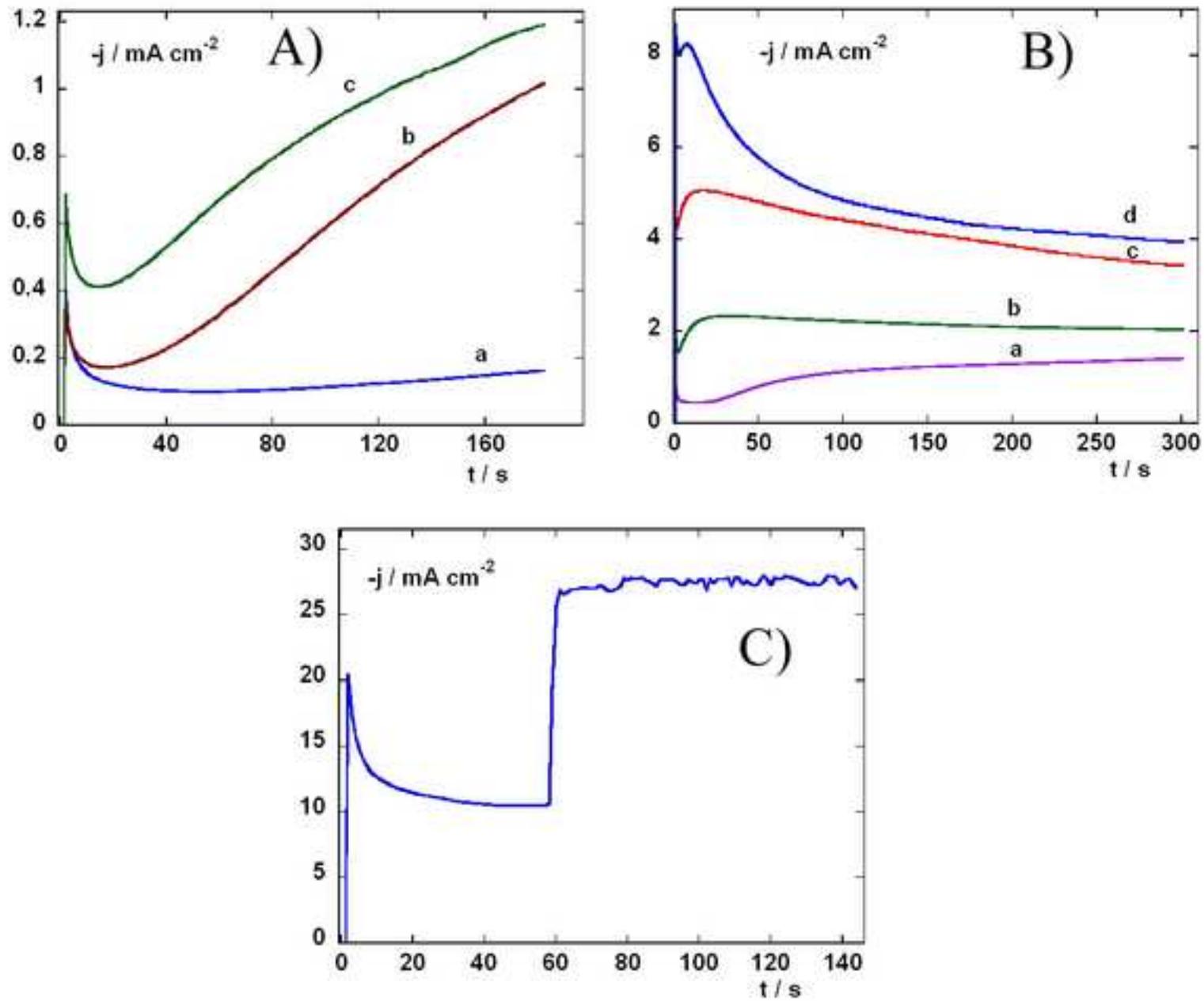


Figure 8

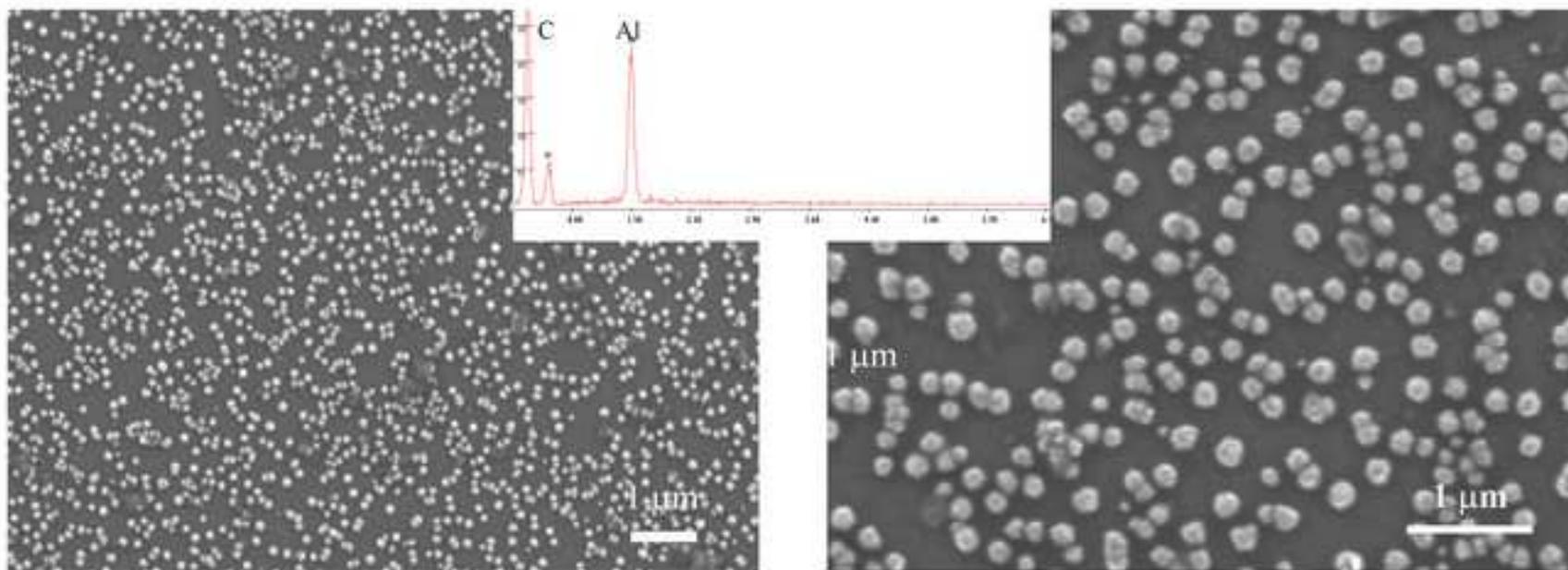


Figure 9

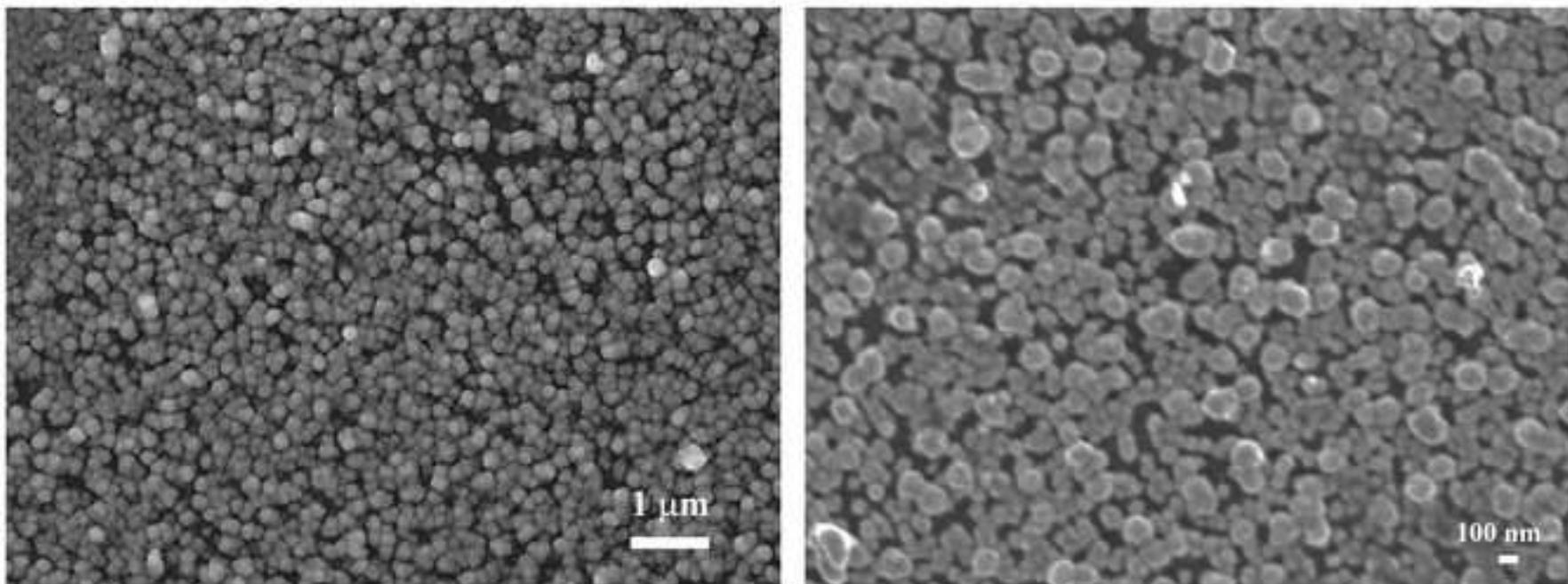


Figure 10