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(54) **METHOD FOR PREPARING METALLIC LITHIUM USING ELECTROLYSIS IN NON-AQUEOUS ELECTROLYTE**

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(57) **ABSTRACT**

The present invention provides a method for preparing metallic lithium by electrolysis using a non-aqueous electrolyte at low temperature. The method for preparing metallic lithium according to the present invention can directly prepare metallic lithium by electrolysis at a low temperature, and enable mass production, and reduce the manufacturing cost due to its simple process and easy control of electrolytic conditions, and thus the method for preparing lithium thin films according to the present invention can be applied in the industry.

FIG. 1

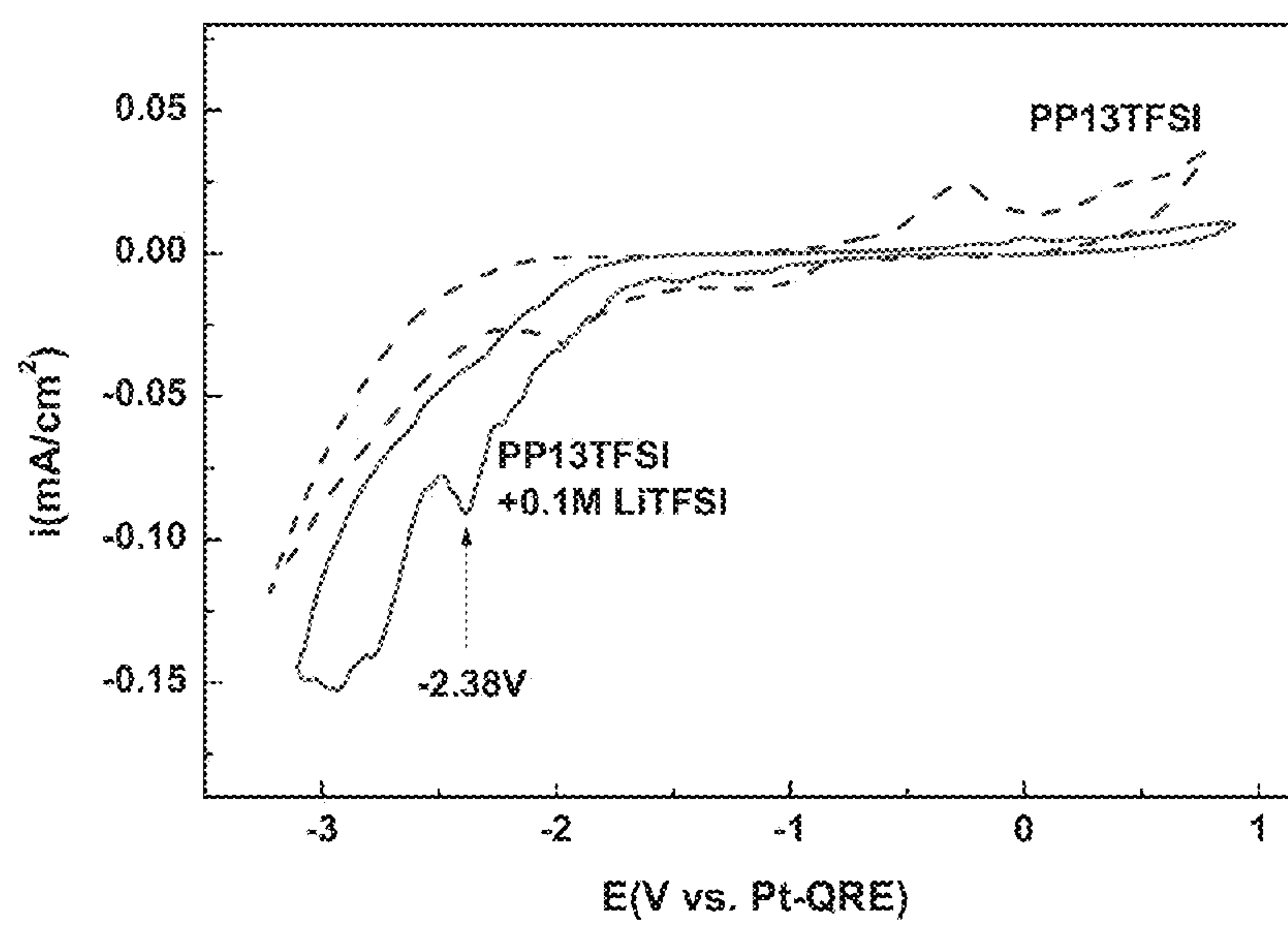


FIG. 2

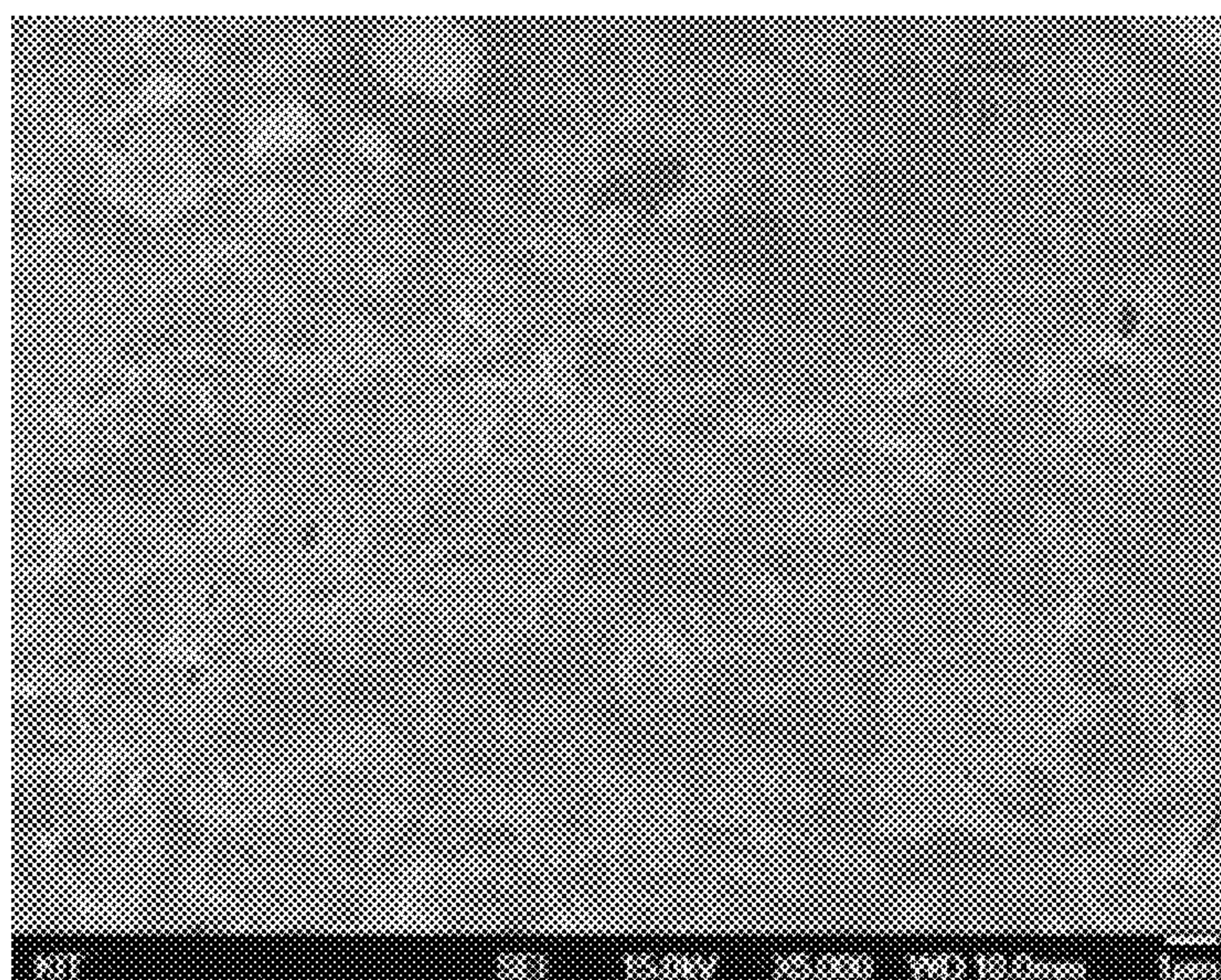


FIG. 3

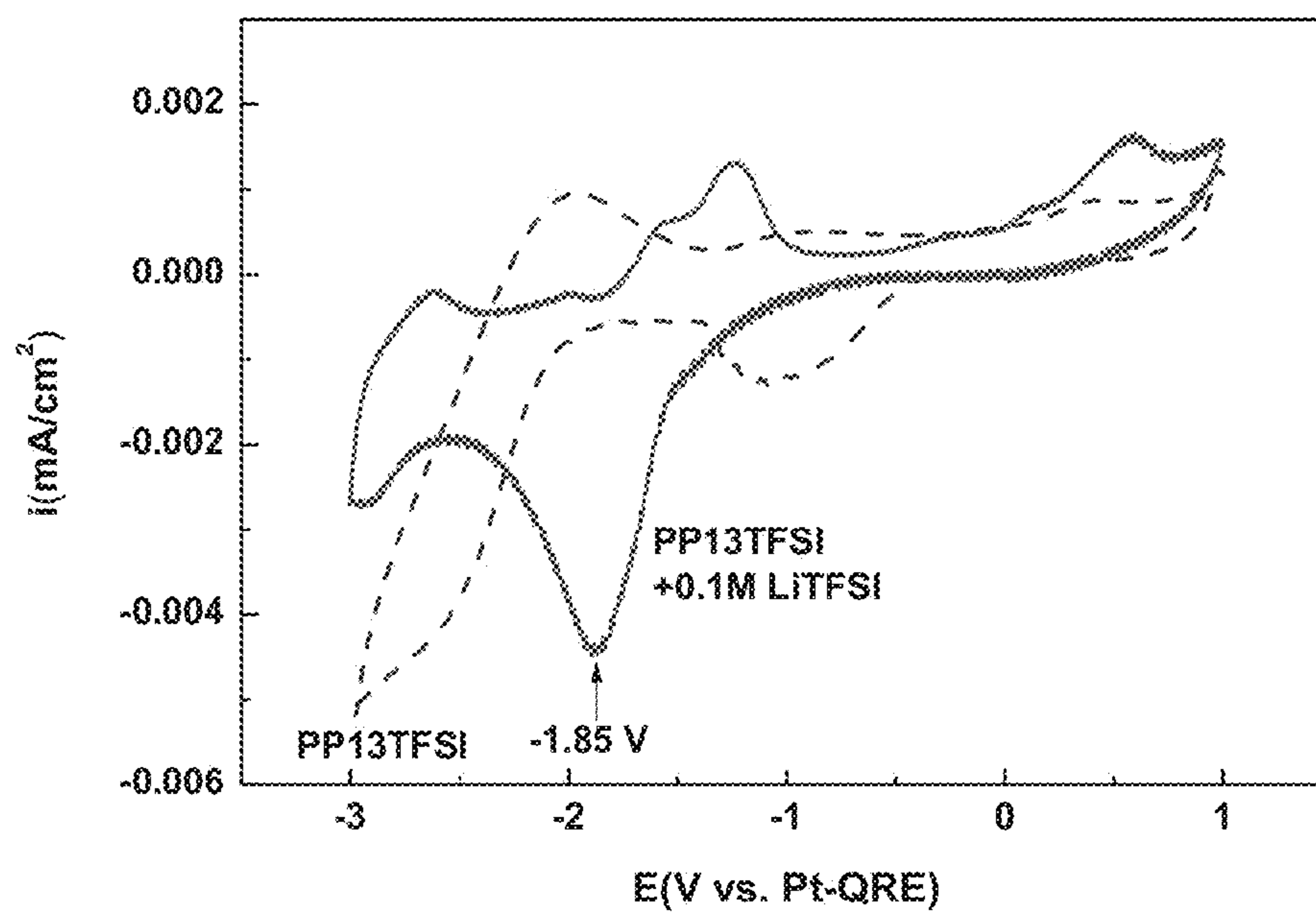


FIG. 4

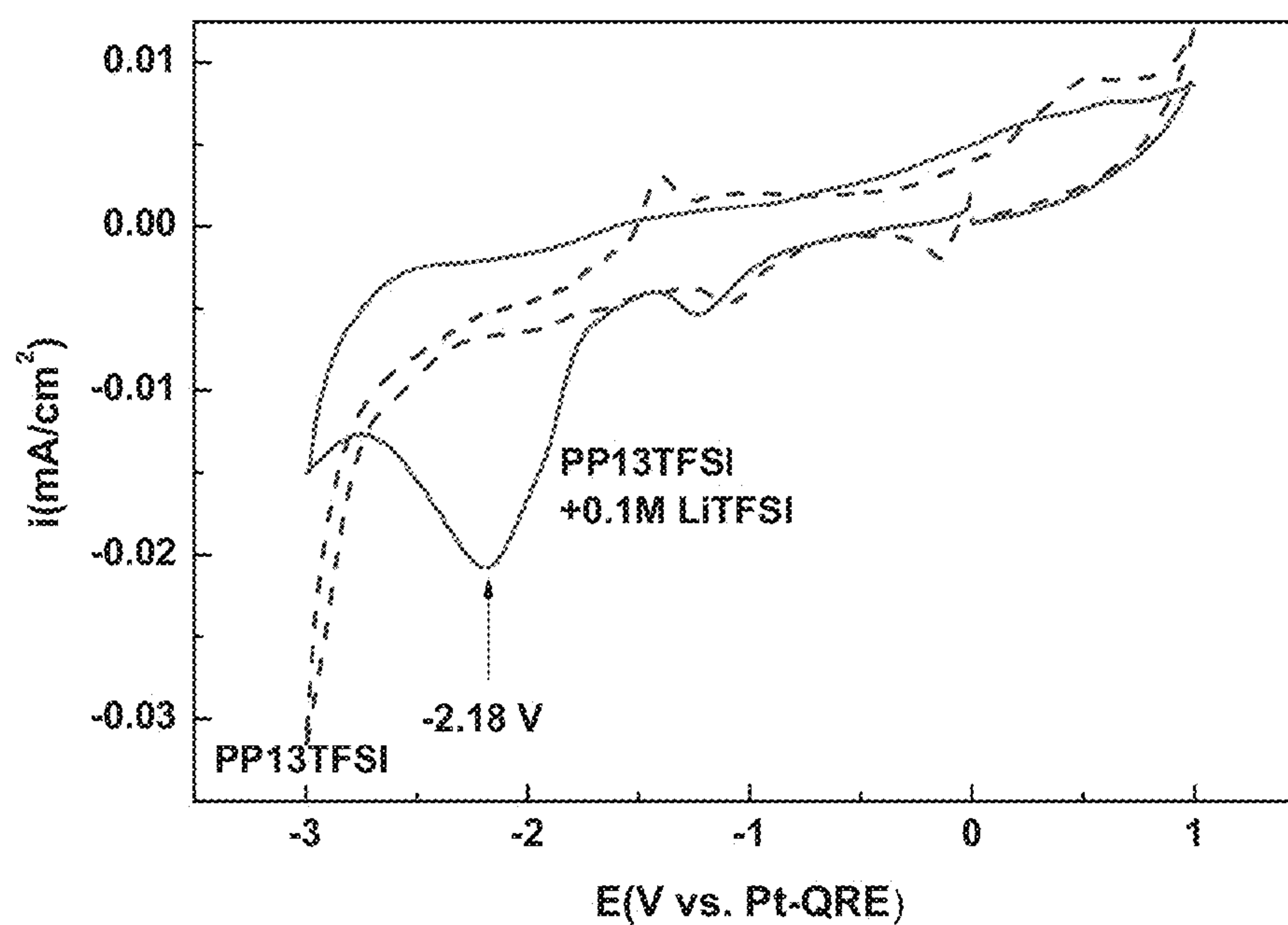


FIG. 5

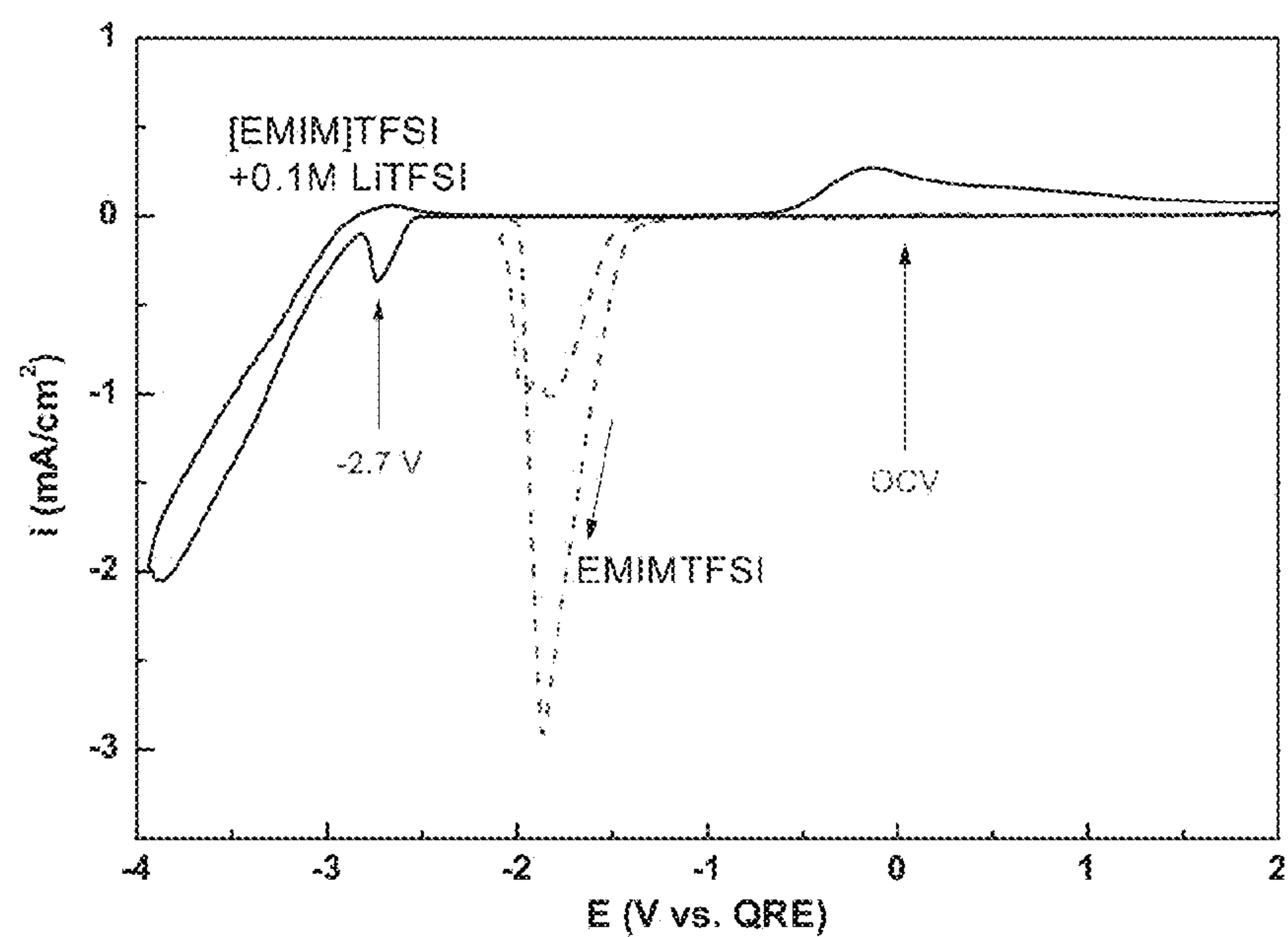


FIG. 6

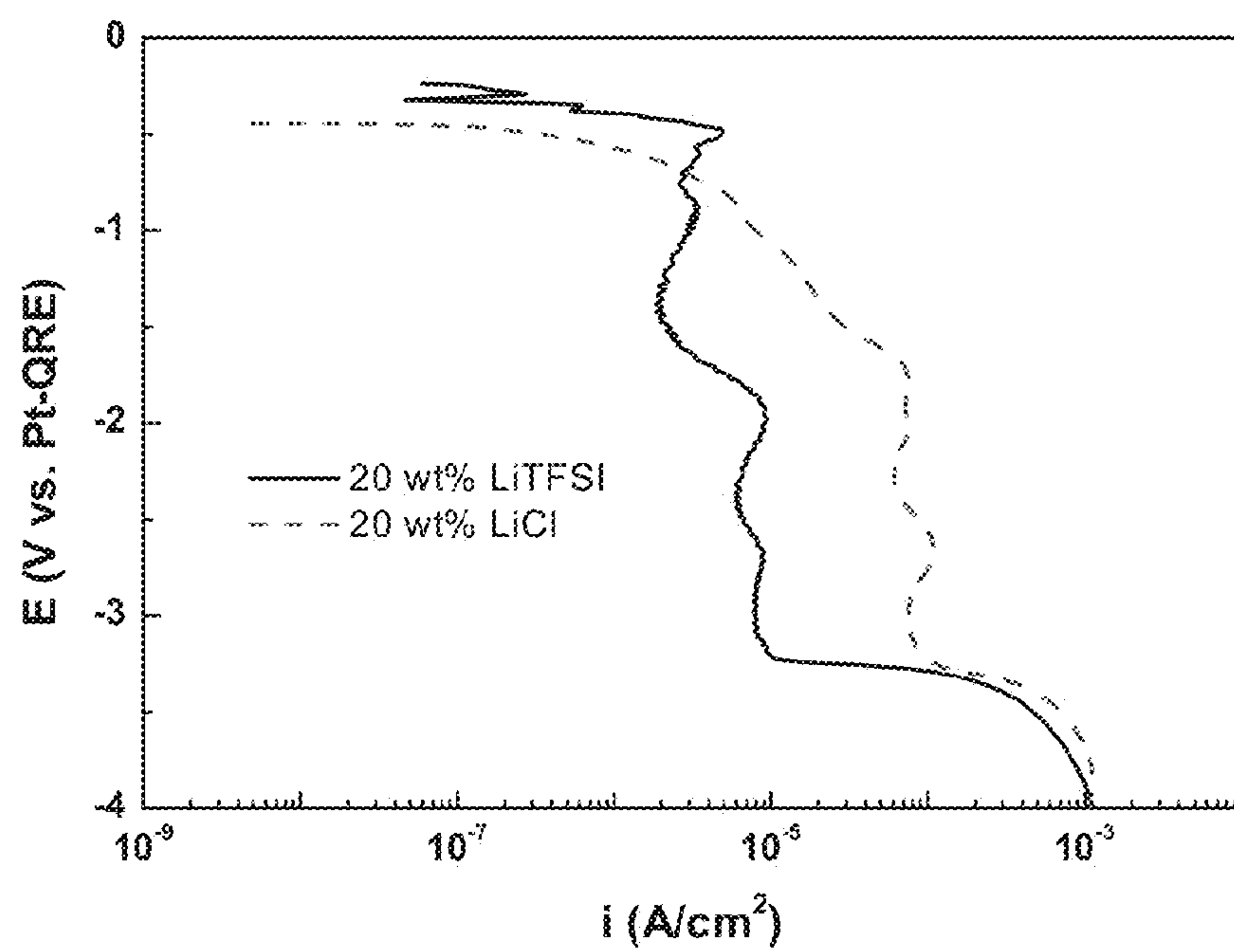




FIG. 7

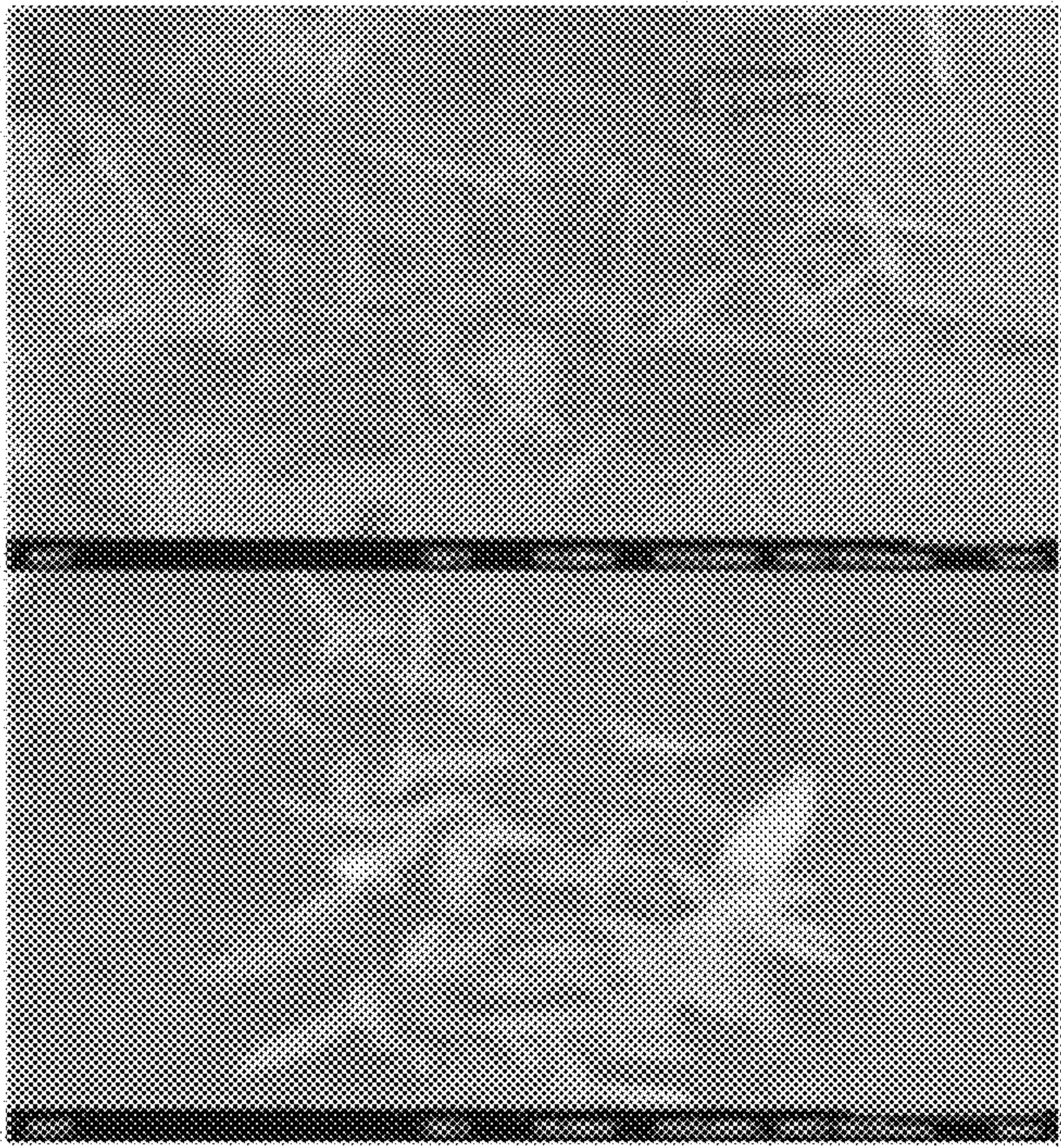


FIG. 8

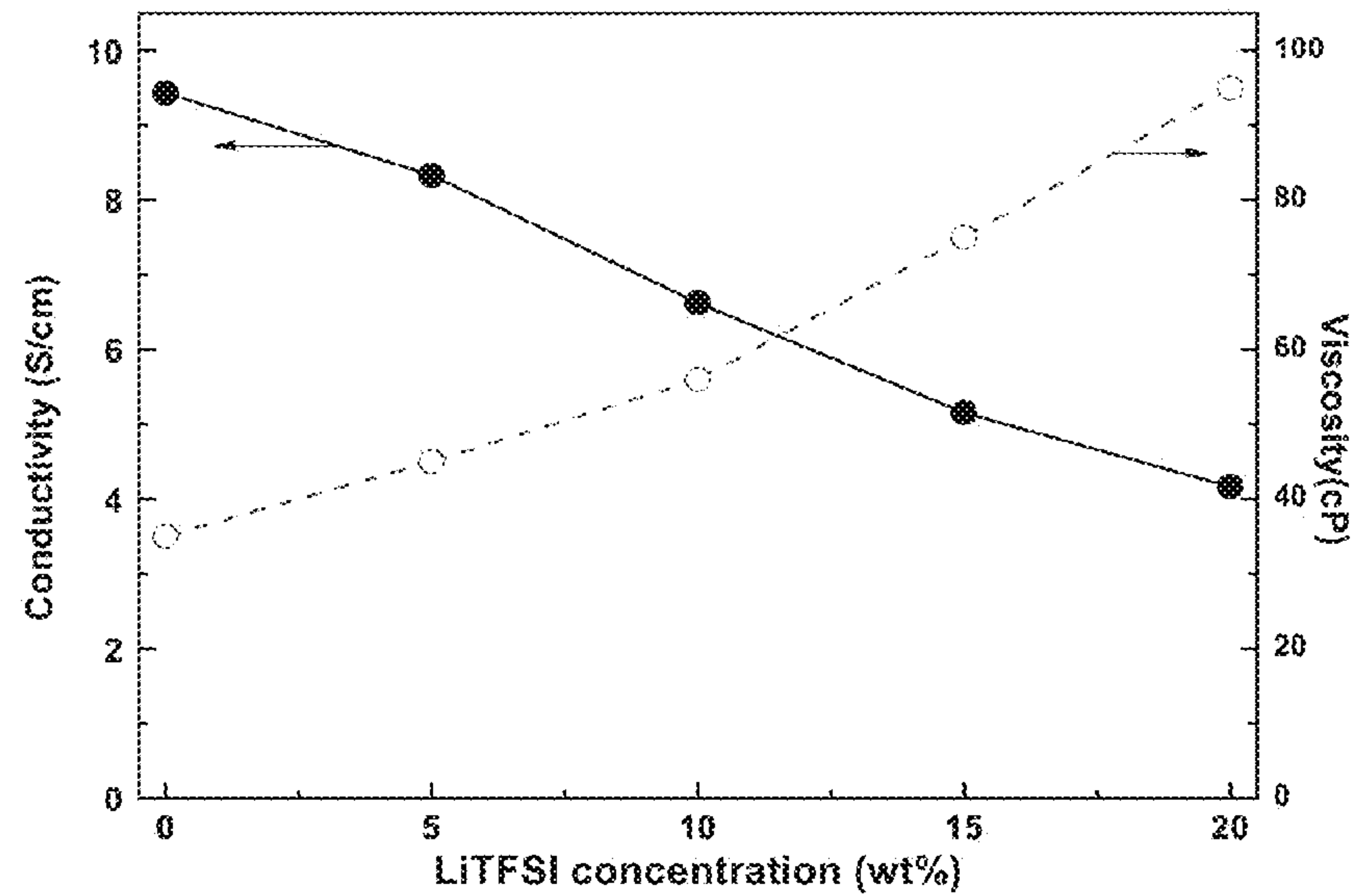


FIG. 9

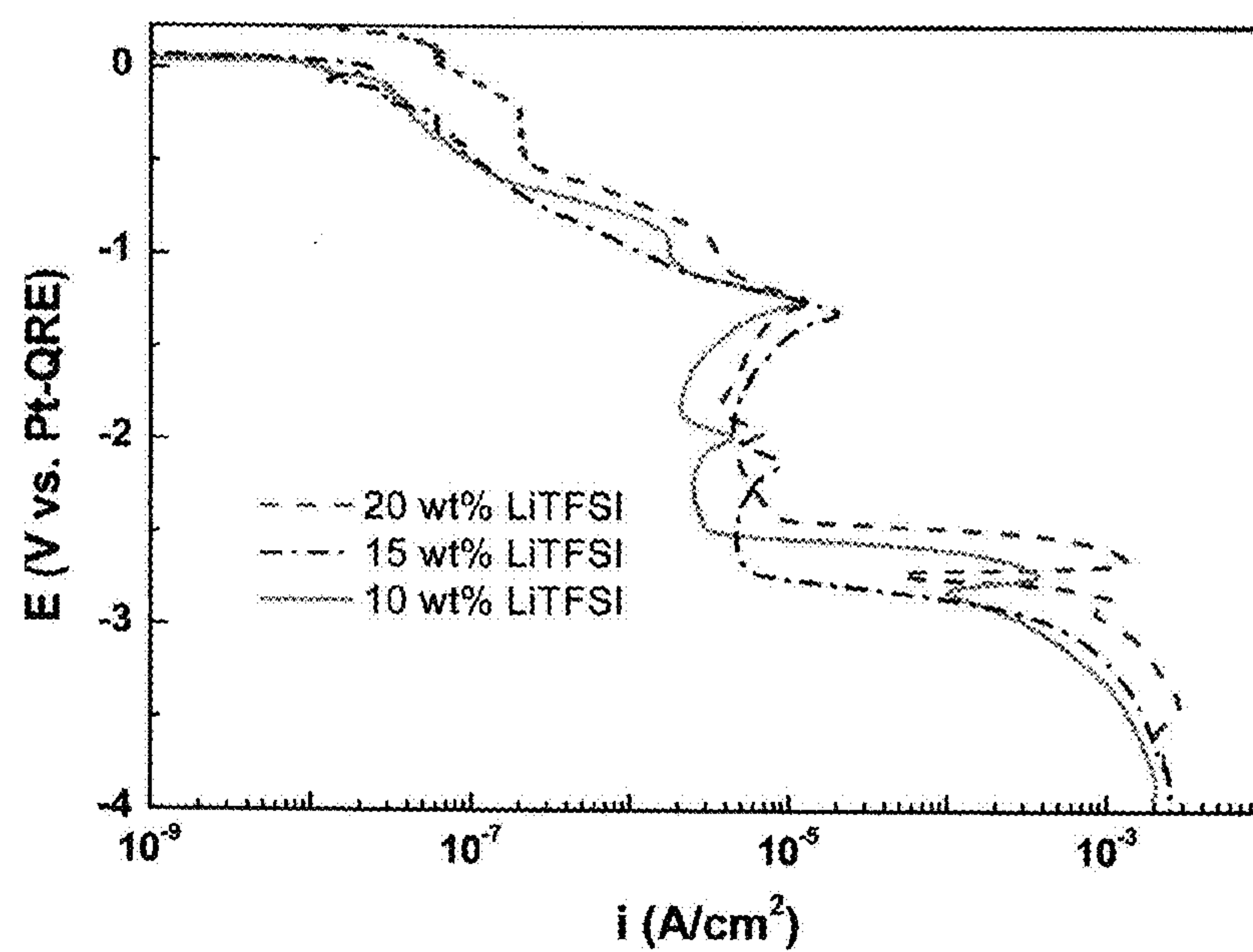


FIG. 10

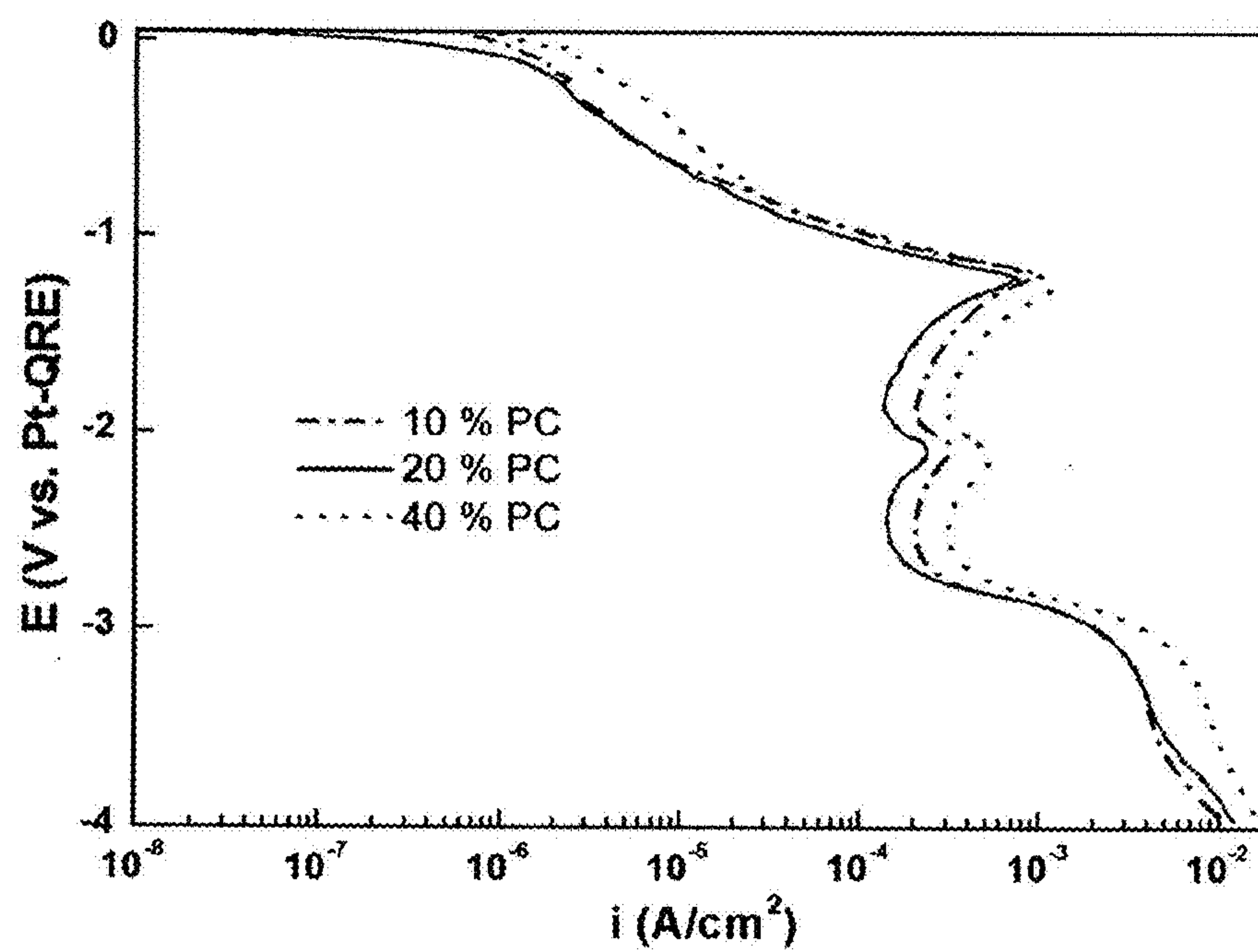




FIG. 11

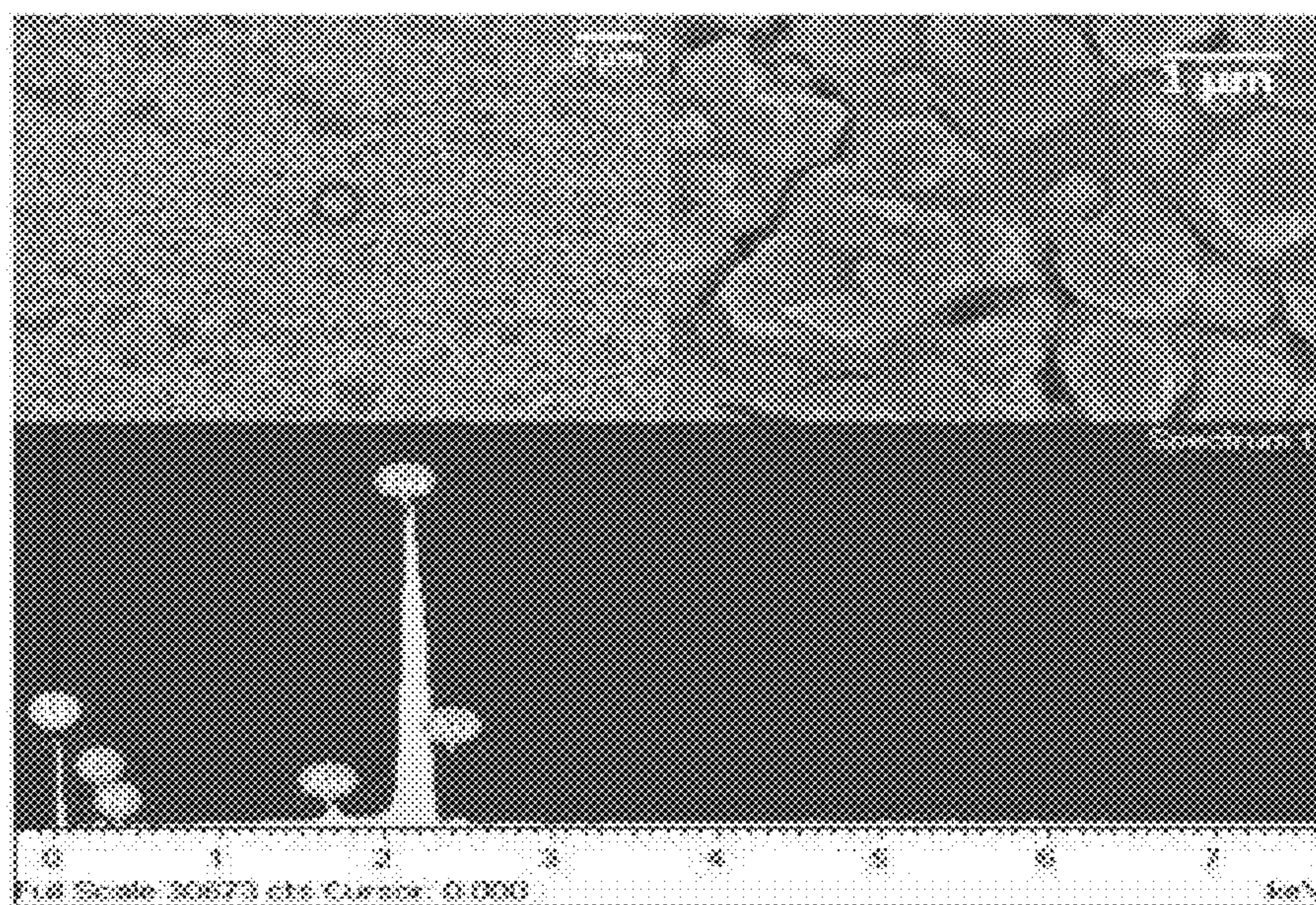


FIG. 12

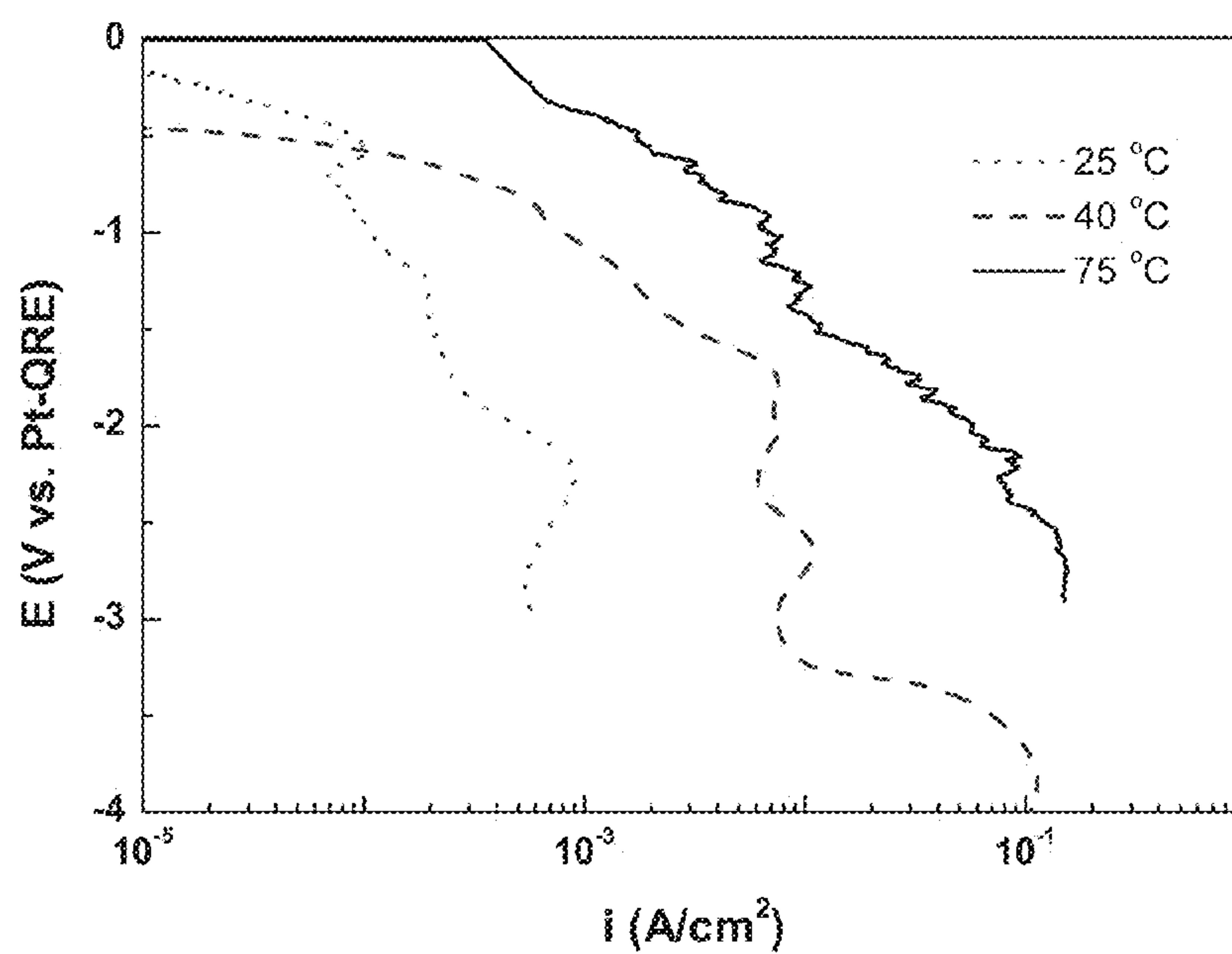
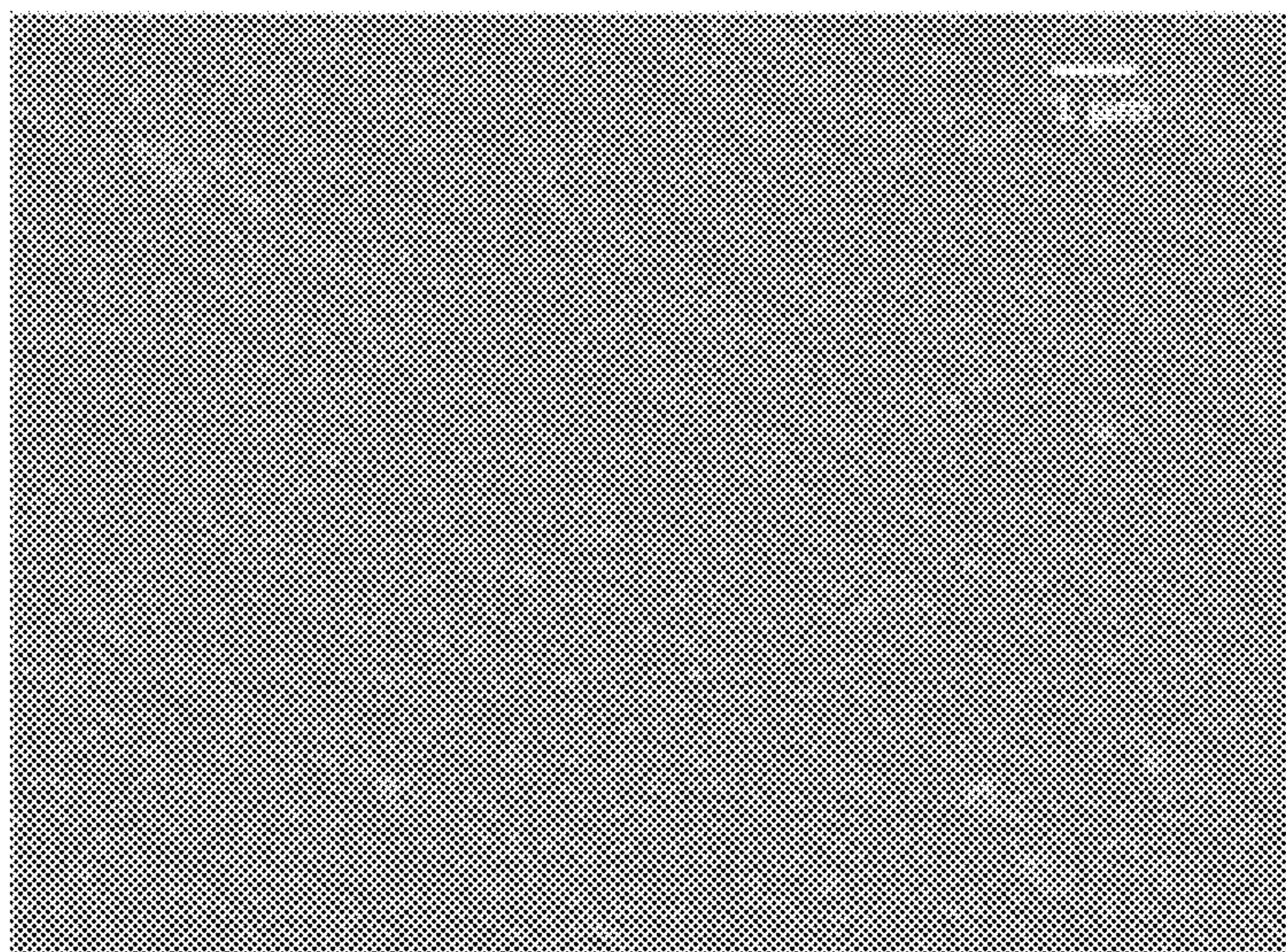




FIG. 13





# METHOD FOR PREPARING METALLIC LITHIUM USING ELECTROLYSIS IN NON-AQUEOUS ELECTROLYTE

## CROSS-REFERENCE TO RELATED PATENT APPLICATION

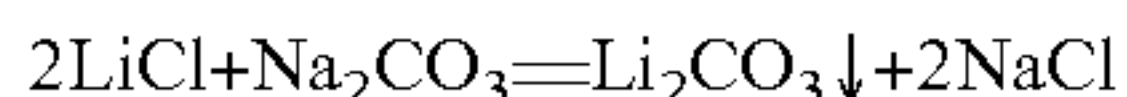
[0001] This application claims the benefit of Korean Patent Application No. 10-2012-0133833, filed on Nov. 23, 2012, in the Korean Intellectual Property Office, the disclosure of which is incorporated herein in its entirety by reference.

## FIELD OF THE INVENTION

[0002] The present invention relates to a non-aqueous electrolysis for directly recovering metallic lithium from lithium-containing ores or waste resources.

## BACKGROUND OF THE INVENTION

[0003] Lithium is a chemical element belonging to the alkali metal group and is soft, silvery-white, and corrosive. Thus, lithium is used in alloys for heat transfer applications, batteries, etc., and thus its demand is significantly increasing. The general procedure for preparation of lithium is as follows. First, lithium carbonate is obtained by evaporating water from a salt solution containing lithium and then adding sodium carbonate thereto. At this time, the salt water is concentrated until the lithium content exceeds 0.5%, and lithium carbonate that is insoluble in water is taken out of the water.



[0004] Lithium carbonate is mixed with hydrochloric acid to be reduced to lithium metal. Carbon dioxide is dispersed into the atmosphere as a gas, and lithium chloride is dissolved in the solution. The resulting solution is concentrated until the lithium chloride forms crystals in a vacuum evaporator.



[0005] Metallic lithium is extracted by molten-salt electrolysis using a eutectic mixture, which comprises 52% lithium chloride and 48% potassium chloride and melts at 352° C., as an electrolyte.



[0006] In the electrolytic process, potassium and sodium as impurities show different behaviors. That is, potassium having a higher standard electrode potential is not readily reduced, but sodium that is reduced to a trace amount increases the reactivity of lithium, thus reducing the stability of metallic lithium. Lithium containing a small amount of impurities such as sodium can be used in organic chemistry but cannot be used in battery applications. In 1855, Robert Bunsen and Augustus Matthiessen extracted larger quantities of pure lithium by molten-salt electrolysis of lithium chloride (LiCl) and, in 1923, Deutsche Metallgesellschaft (today: GEA Group) started commercial production of lithium by electrolyzing molten salts of lithium chloride and potassium chloride (KCl).

[0007] Recently, studies on the recovery of lithium from seawater have been actively conducted worldwide. A method for recovery of lithium comprises adsorbing alkali metals by ion exchange, stripping with an aqueous solution, and precipitating carbonate, but eventually there is no technology other than the above-mentioned molten-salt electrolysis to prepare metallic lithium. However, the molten-salt electrolysis is a high-temperature process, which has high energy

consumption, requires high production costs, and has a significant effect on the environment, and thus various studies for solving these problems have been conducted.

[0008] A study of preparing metallic lithium thin films by room-temperature electrolysis using a polymer electrolyte (T. Matsui and K. Takeyama, 1995: Lithium deposit morphology from polymer electrolytes, *Electrochimica Acta*, 40(13-14), pp. 2165-2169), a study of the redox behavior of lithium in organic solvents with lithium halides containing  $\text{LiPF}_6$  or  $\text{LiBF}_4$  (X. Yang, Z. Wen, X. Zhu and S. Huang, 2005: Electrodeposition of lithium film under dynamic conditions and its application in all-solid-state rechargeable lithium battery, *Solid State Ionics*, 176(11-12), pp. 1051-1055), etc. have been conducted. However, the reaction rate of this electrolysis is very low, lithium is deposited into needle-like shapes, or halide anions react with water to act as impurities in deposits, making it very difficult to control the crystallinity and purity of the final product.

[0009] Recently, composites such as room-temperature ionic liquids, which exhibit high chemical and electrochemical stability and high electrical conductivity as well, have been developed and applied to the room-temperature electrolysis of lightweight, highly active metals, which was impossible in aqueous electrolysis. In particular, a research result on the preparation of metallic lithium thin films has been published (H. Ohno and M. Yoshizawa, 2002: Ion conductive characteristics of ionic liquids prepared by neutralization of alkylimidazoles, *Solid State Ionics*, 154-155, pp. 303-309). Moreover, studies on the interaction of these room-temperature ionic liquids and lithium are widely applied to the development of secondary batteries using metallic lithium as an electrode material. Sakaebe confirmed the potential of 1-methyl-propylpiperidinium bis(trifluoromethylsulfonyl) imide (PP13TFSI) with dissolved LiTFSI used as an electrolyte for a secondary battery (H. Sakaebe, H. Matsumoto, and K. Tatsumi, 2007: Application of room temperature ionic liquids to Li batteries, *Electrochimica Acta*, 53(3, 20), p 1048-1054). 1-ethyl-3-methyl imidazolium (EMIM)-series room temperature ionic liquids such as [EMIM] $\text{BF}_4$  have been widely used in the fields of plating, thin-film fabrication, etc. in addition to electrolytic applications since their viscosity and electrical conductivity are significantly enhanced (J. S. Wilkes and M. J. Zaworotko, 1992: Air and water stable 1-ethyl-3-methylimidazolium based ionic liquids, *Chem. Commun.*, 54, pp. 965-967) and their electrochemical stability is significantly improved (H. Sakaebe and H. Matsumoto, 2005: *Electrochemical Aspects of Ionic Liquids*, edited by H. Ohno, John Wiley and Sons Inc., Hoboken, N.J., p. 173; B. Garcia, S. Lavall'ee, G. Perron, C. Michot, and M. Armand, 2004: Room temperature molten salts as lithium battery electrolyte, *Electrochimica Acta*, 49, pp. 4583-4588).

[0010] The above-mentioned preparation methods of lithium require high installation costs, complex processes, and much energy, but the electrolysis, a general method using electrochemistry, is a relatively simple process because the deposition properties can be controlled by the composition of the electrolyte and the control of current density and voltage. However, it is possible to obtain high purity lithium only when the partial incorporation of a solvent that constitutes the electrolyte or anions of lithium salts used as a lithium source in the reduction can be controlled.

[0011] Thus, the need to develop optimal conditions for electrolysis in a method for preparing metallic lithium by



electrolysis using a simple process compared to other complex processes is urgently required.

#### SUMMARY OF THE INVENTION

**[0012]** The present inventors have studied a method for recovery of metallic lithium by non-aqueous electrolysis at ambient temperature and found that the electrolytic efficiency of lithium was significantly improved and the stability of metallic lithium deposits was also improved by the use of a specific non-aqueous electrolyte, thus completing the present invention.

**[0013]** Therefore, an object of the present invention is to provide a method for preparing metallic lithium using electrolysis in a non-aqueous electrolyte, which can facilitate the manufacturing process at low temperature using a non-aqueous electrolyte, easily control the properties of lithium deposits due to easy control of electrolytic conditions, reduce the energy consumption, and cause little or no environmental pollution.

**[0014]** Another object of the present invention is to provide a metallic lithium prepared by the above method.

#### BRIEF DESCRIPTION OF THE DRAWINGS

**[0015]** The above and other features and advantages of the present invention will become more apparent by describing in detail exemplary embodiments thereof with reference to the attached drawings in which:

**[0016]** FIG. 1 shows cyclic voltammograms obtained using gold as a working electrode in an electrolyte with 0.1M LiTFSI dissolved in PP13TFSI.

**[0017]** FIG. 2 shows an SEM image of the surface after performing an electrolytic reduction test by potentiostatic method in PP13TFSI electrolyte with dissolved 0.5 M LiTFSI.

**[0018]** FIG. 3 shows cyclic voltammograms measured using platinum as a working electrode.

**[0019]** FIG. 4 shows cyclic voltammograms measured using copper as a working electrode.

**[0020]** FIG. 5 shows electrochemical properties obtained using [EMIM]TFSI with a dissolved lithium salt as an electrolyte.

**[0021]** FIG. 6 shows cyclic voltammograms illustrating electrolytic properties of lithium measured using [EMIM]TFSI with dissolved LiTFSI and LiCl as electrolytes.

**[0022]** FIG. 7 shows surface images of lithium prepared by potentiostatic method in an electrolyte with dissolved LiCl.

**[0023]** FIG. 8 shows the viscosity and electrical conductivity of an electrolyte with a dissolved lithium salt in [EMIM]TFSI.

**[0024]** FIG. 9 shows cyclic voltammograms illustrating electrolytic properties depending on the concentration of lithium in [EMIM]TFSI electrolytes.

**[0025]** FIG. 10 shows cyclic voltammograms depending on the amount of PC added to an electrolyte.

**[0026]** FIG. 11 shows surface images of lithium prepared by potentiostatic method in [EMIM]TFSI electrolyte with improved properties by the addition of PC.

**[0027]** FIG. 12 shows changes in electrical conductivity of an electrolyte depending on temperature.

**[0028]** FIG. 13 shows a surface image of lithium deposited by applying a pulsed current.

#### DETAILED DESCRIPTION OF THE INVENTION

**[0029]** The present invention provides a method for preparing metallic lithium, the method comprising the steps of:

**[0030]** (a) placing an electrolytic cell including conductive electrodes in a non-aqueous conductive solvent with a dissolved lithium salt in a high purity inert gas atmosphere; and

**[0031]** (b) applying an electric power to the electrolytic cell in step (a) such that lithium is reduced at a cathode and metallic lithium is deposited on the surface of the cathode.

**[0032]** Moreover, the present invention provides metallic lithium prepared by the above method.

**[0033]** Hereinafter, the present invention will be described in detail.

**[0034]** In the method for preparing metallic lithium, the basic structure of the electrolytic cell for electrolytic reduction in step (a) is a ternary electrode system in which a reference electrode for precisely monitoring the voltage applied to a cathode is added to an electrolytic cell comprising a working electrode and a relative electrode.

**[0035]** The electrodes may comprise any conductive metal and may preferably comprise at least two metals selected from the group consisting of gold, platinum, and copper, but not limited thereto.

**[0036]** In step (a), the high purity inert gas may comprise at least one selected from the group consisting of nitrogen, helium, argon, neon, and xenon and may preferably comprise argon. The production of metallic lithium in a high purity inert gas atmosphere provides the effect of preventing reoxidation of lithium.

**[0037]** In step (a), the lithium salt may comprise at least one selected from the group consisting of LiTFSI, LiCl, LiF, LiPF<sub>6</sub>, and LiBF<sub>4</sub>. The lithium salt may be dissolved in a maximum amount of 30 wt % with respect to the total weight and does not cause any reoxidation of reduced lithium due to the absence of oxygen.

**[0038]** In step (a), any non-aqueous conductive solvent capable of dissolving the lithium salt may be used as an electrolyte. The non-aqueous conductive solvent is a non-aqueous conductive solvent containing a bis(trifluoromethylsulfonyl)imide (TFSI) anion and may comprise at least one selected from the group consisting of 1-Butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide ([BMPy]TFSI), 1-methyl-propylpiperidinium bis(trifluoromethylsulfonyl)imide (PP13TFSI), and 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide ([EMIM]TFSI), but not limited thereto.

**[0039]** Moreover, the non-aqueous conductive solvent may further comprise propylene carbonate (PC), dichloromethane (DCM), tetrahydrofuran (THF), dicyanamide (DCA), or N-methylpyrrolidone (NMP). These materials have very low viscosity, have no effect on the dissociation of lithium, and improve the electrical conductivity of the electrolyte.

**[0040]** The method for preparing metallic lithium may further comprise, before step (a), the steps of: (a') washing the electrodes and the cell with a mixed solution of sulfuric acid and hydrogen peroxide; and (a'') drying the non-aqueous solvent at 80 to 120° C. for 20 to 30 hours. The sulfuric acid and hydrogen peroxide in step (a') may preferably be mixed at 1:1 vol %, and impurities can be removed from the electrodes and the cell by performing this step. A small amount of water contained in the non-aqueous solvent can be removed by performing step (a'').

**[0041]** In step (b), the lithium is reduced at a cathode and metallic lithium is deposited on the surface of the cathode by



applying an electric power to the electrolytic cell. When placing two metal electrodes in the electrolyte with a dissolved lithium salt and applying an electric power thereto in the same manner as the typical electroplating, the reduction of lithium occurs at the cathode, and the formation of metallic lithium deposits occurs on the surface of the electrode.

**[0042]** The reduction of lithium may be performed by pulsed plating such that the lithium is deposited. The pulsed plating may be performed by periodically applying a current of 10 to 100 mA/cm<sup>2</sup> for 0.001 to 0.1 minutes and 1 to 5 mA/cm<sup>2</sup> for 1 to 60 minutes, and the average current density may preferably be maintained at 1 to 5 mA/cm<sup>2</sup>. When the pulsed plating is performed in the above manner, it can be seen that the lithium particles with a size of less than about 0.1 μm were uniformly deposited compared to the lithium reduction with a direct current.

**[0043]** The method for preparing metallic lithium may further comprise, after step (b), the step of performing heat treatment on the deposited lithium at 800 to 900° C. for 30 to 90 minutes in an inert gas atmosphere. The inert gas may comprise nitrogen, helium, argon, neon, and xenon, but not limited thereto. The heat treatment step provides the effect of removing impurities from the lithium and the effect of stabilizing the deposited lithium.

**[0044]** As described above, according to the method for preparing metallic lithium of the present invention, the metallic lithium can be directly prepared by electrolysis at ambient temperature, and thus the process is easy compared to other complex processes. Moreover, the method is a low temperature process, and thus mass production is possible and the cost is reduced. Furthermore, the method for preparing metallic lithium of the present invention, it is possible to facilitate the manufacturing process, easily control the properties of lithium thin films due to easy control of electrolytic conditions, and continuously prepare the metallic lithium by repeatedly dissolving the lithium salt.

**[0045]** Hereinafter, preferred examples will be provided to facilitate understanding of the present invention. However, the following examples are provided to only to make it easier to understand the present invention, and the present invention is not limited by the following examples.

#### Example 1

##### Electrolytic Reduction of Lithium

**[0046]** In order to determine the reduction of lithium according to the present invention, the following tests were performed.

**[0047]** An electrolytic cell with a ternary electrode system was used for the electrolytic reduction of lithium, in which a working electrode was gold and an opposite electrode was platinum. An electrolyte with LiTFSI dissolved in PP13TFSI was used as a non-aqueous conductive solvent. The ternary electrode system refers to the structure in which a reference electrode for precisely monitoring the voltage applied to a cathode is added to an electrolytic cell comprising a working electrode and a relative electrode.

**[0048]** Before the tests, all the electrodes and the electrolytic cell were washed with a mixed solution of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) at a mixed ratio of 50:50 vol %, and all the non-aqueous solvents were dried at a 100° C. vacuum oven for 24 hours and used for the electrolysis.

**[0049]** The redox current of lithium depending on the voltage was measured by cyclic voltammetry (CV).

**[0050]** The change in current was measured from the equilibrium potential to -3 to 1 V at a scanning rate of 10 mV/s and in a direction from the cathode to the anode and converted to current density, thus investigating the electrolytic reduction characteristics of lithium. The cyclic voltammograms in an electrolyte with 0.1 M LiTFSI dissolved in PP13TFSI are shown in FIG. 1.

**[0051]** As shown in FIG. 1, when comparing the behavior in PP13TFSI with dissolved 0.1 M LiTFSI and the behavior in PP13TFSI without lithium salt, a reduction current peak is observed at -2.4 V (vs. Pt-QRE) which is within the stable potential range of PP13TFSI, and it is assumed that this was caused by the reduction of lithium. Moreover, it was found that the peak interpreted as the reduction current of lithium was at a potential higher than the reduction limit potential, and thus the possibility that impurities were introduced in the reduction reaction was low.

**[0052]** In order to analyze the morphology, composition, and crystallinity of the metallic lithium prepared by the electrolysis, the electrolytic reduction tests were performed by potentiostatic method (at -2.4 V vs. Pt-QRE) in PP13TFSI electrolyte with 0.5 M LiTFSI, and the surface analysis result is shown in FIG. 2.

**[0053]** As shown in FIG. 2, the morphology of the deposits shows a porous structure in which fine lithium particles are aggregated to a size of approximately 1 μm and pores are generally present.

**[0054]** Moreover, according to the EDS analysis results of the deposits, it can be seen that the deposits are composed of lithium, gold, and oxygen. The lithium deposits were obtained in the stable potential range of the electrolyte which was confirmed from the cyclic voltammograms, and thus other impurities than the working electrode were not observed, but a large amount of oxygen was detected. All tests for the measurement of the reduction of lithium and the properties of ionic liquids were performed in a glove box under an argon atmosphere, and the possibility of oxidation of lithium in the electrolysis process is low. Moreover, since any water that may remain was removed from the ionic liquids by drying before the tests, it is considered that the detected oxygen resulted from the oxidation occurring on the surface by exposure to the outside when the samples were prepared and moved to analysis instruments, and it was found that pure lithium was reduced as the components of the electrolyte were not detected.

#### Experimental Example 1

##### CV Measurement Depending on Working Electrodes

**[0055]** The CV results measured when platinum was used as the working electrode in the same electrolytic cell and electrolyte as those in Example 1 are shown in FIG. 3.

**[0056]** As shown in FIG. 3, the peak interpreted as the reduction of lithium was observed at -1.85 V (vs. Pt-QRE), and the peaks interpreted as the oxidation and reduction of ionic liquids were also observed, and thus it was found that the stability of PP13TFSI as the solvent was very low.

**[0057]** Moreover, the CV results measured using copper as the working electrode in the same electrolyte are shown in FIG. 4.

**[0058]** As shown in FIG. 4, it can be seen that the stability of PP13TFSI is similar to the position of the voltage (-2.18 V



vs. Pt-QRE) at which the lithium is reduced, but the reduction current is lower than that of gold, indicating that the catalytic performance of gold is most excellent in the electrolytic reduction of metallic lithium.

#### Experimental Example 2

##### Replacement of Non-Aqueous Conductive Solvents

**[0059]** The electrolytic properties of lithium when gold was used as the working electrode in the same electrolytic cell as that in Example 1 and [EMIM]TFSI with a dissolved lithium salt was used as the conductive electrolyte were measured by cyclic voltammetry. The measurement results of electrochemical properties in [EMIM]TFSI are shown in FIG. 5.

**[0060]** As shown in FIG. 5, it can be seen that the reduction peak of lithium is  $-2.7$  V which is slightly lower than  $-2.4$  V in PP13TFSI, indicating that other non-aqueous conductive solvents capable of dissolving the lithium salt can be used for the recovery of metallic lithium. Moreover, it can be seen that the stable reduction region of [EMIM]TFSI was shifted from about  $-2$  V to about  $-3$  V in the negative direction by the addition of LiTFSI. However, the cations of the solvent, which determine the cathode limit potential, had the lowest stable cathode potential in EMIM, and the cathode reactivity was most stable in PP13. However, it was found that PP13 caused a decrease in electrical conductivity of the electrolyte due to high viscosity and a corresponding decrease in electrolytic efficiency.

#### Experimental Example 3

##### Characterization of Electrolytic Reduction of Lithium Depending on Lithium Salts

**[0061]** In order to determine the electrolytic reduction characteristics of lithium depending on the type of lithium salt in the same electrolytic cell as that in Experimental Example 2, intermediate products such as LiCl, LiF,  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ , LiOH,  $\text{Li}_2\text{CO}_3$ , etc. other than LiTFSI were dissolved in [EMIM]TFSI. It was found that LiOH,  $\text{Li}_2\text{CO}_3$ , etc. were not suitable as starting materials because they were less dissolved and oxygen was present when they were dissolved, thus causing reoxidation of reduced metallic lithium. However, LiCl, LiF,  $\text{LiPF}_6$ , and  $\text{LiBF}_4$  were suitable for starting materials because they were dissolved in a maximum amount of 30 wt % with respect to the total weight of the electrolyte. The electrolytic properties of lithium in [EMIM]TFSI with dissolved LiTFSI and LiCl as electrolytes were measured by potentiodynamic method, and the results are shown in FIG. 6.

**[0062]** As shown in FIG. 6, it can be seen that the reduction current in the electrolyte with dissolved LiCl is as low as  $1/100$  of that in [EMIM]TFSI with dissolved LiTFSI, indicating that the use of a lithium salt with a high reduction current can improve electrolytic efficiency.

**[0063]** The surface images of lithium prepared by potentiostatic method in the electrolyte with dissolved LiCl are shown in FIG. 7.

**[0064]** As shown in FIG. 7, it can be seen that the deposits having a length of approximately  $1.5 \mu\text{m}$  are aggregated into needle-like shapes, which is very similar behavior to the results generally observed in the redox reaction of lithium in secondary batteries or in high-temperature electrolysis of lithium. Moreover, the needle-like shapes of the deposits adversely affect the electrolytic process compared to the LiTFSI electrolyte, and thus it is considered that a change in

morphology of deposits to spherical shapes by optimizing the electrolytic conditions should be made to commercialize the room temperature electrolysis of lithium. Thus, it was found that it is possible to obtain spherical deposits by using LiTFSI as a starting material instead of LiCl and obtain finer deposits by applying a current or voltage in pulsed conditions.

#### Experimental Example 4

##### Characterization of Electrolytic Reduction of Lithium Depending on Lithium Concentration

**[0065]** The viscosity and electrical conductivity of an electrolyte with a dissolved lithium salt in [EMIM]TFSI were measured, and the results are shown in FIG. 8.

**[0066]** As shown in FIG. 8, it can be seen that the electrical conductivity of [EMIM]TFSI decreases as the LiTFSI concentration increases, from which it can be determined that the increase in viscosity is greater than the increase in ions as the LiTFSI concentration increases.

**[0067]** Moreover, the electrolytic properties depending on the concentration of lithium in [EMIM]TFSI electrolytes are shown in FIG. 9.

**[0068]** As shown in FIG. 9, it can be seen that the reduction current increases as the lithium concentration increases, from which it can be determined that the electrolytic efficiency can be improved by maintaining the lithium concentration as high as possible during the recovery of lithium from the solution by electrolytic reduction.

#### Experimental Example 5

##### Measurement of Electrical Conductivity of Electrolyte Due to Addition of Additional Solvents

**[0069]** The electrolytic properties of lithium when gold was used as the working electrode in the same electrolytic cell as that in Experimental Example 5 and [EMIM]TFSI with a dissolved lithium salt and polypropylene carbonate (PC) was used as the conductive electrolyte were measured by cyclic voltammetry. The CV behaviors depending on the amounts of PC added are shown in FIG. 10.

**[0070]** As shown in FIG. 10, it can be seen that the reduction current of lithium increases as the amount of PC added increases, from which it can be determined that the effect of improving the physical properties such as electrical conductivity can be obtained from a binary electrolyte containing a solvent such as PC having a low viscosity and the effect of improving the electrolytic properties such as the increase in reduction current can be obtained. Thus, it can be seen that the electrolytic properties of lithium are significantly improved in the binary electrolyte with improved electrolytic properties such as dichloromethane (DCM), dicyanamide (DCA), N-methylpyrrolidone (NMP), tetrahydrofuran (THF), etc. in addition to PC.

**[0071]** The surface images of lithium prepared by potentiostatic method in [EMIM]TFSI electrolyte with improved properties by the addition of PC are shown in FIG. 11.

**[0072]** As shown in FIG. 11, it can be seen that pellet-shaped lithium deposits with a size of  $1 \mu\text{m}$  are uniformly deposited.



## Experimental Example 6

Measurement of Electrical Conductivity of  
Electrolyte Depending on Temperature

**[0073]** The electrolytic properties of lithium depending on the temperature when gold was used as the working electrode in the same electrolytic cell as that in Experimental Example 5 and [EMIM]TFSI with a dissolved lithium salt and 40% PC was used as the conductive electrolyte were measured, and the change in electrical conductivity of the electrolyte depending on the temperature are shown in FIG. 12.

**[0074]** As shown in FIG. 12, it can be seen that the reduction current of lithium increases as the temperature increases, from which it can be determined that the increase in temperature can improve the electrical conductivity in the same electrolyte, increase the reduction rate of lithium, and improve the electrolytic properties.

## Experimental Example 7

## Reduction of Lithium Depending on Pulsed Current

**[0075]** In order to improve the deposition properties of lithium in the same electrolytic conditions as Experimental Example 6, the lithium reduction was performed by applying a pulsed current. The pulsed current was periodically applied at a pulsed current density of 10 to 100 mA/cm<sup>2</sup> for 0.001 to 0.1 minutes and at a pulsed current density of 1 to 5 mA/cm<sup>2</sup> for 1 to 60 minutes, and the average current density was maintained at 1 to 5 mA/cm<sup>2</sup>. The surface image of lithium deposited by periodically applying a pulse current at 100 mA/cm<sup>2</sup> for 0.1 minutes and at 1 mA/cm<sup>2</sup> for 20 minutes are shown in FIG. 13.

**[0076]** As shown in FIG. 13, it can be seen that the lithium particles with a size of less than about 0.1 μm were uniformly deposited compared to the lithium reduction with a direct current.

**[0077]** As described above, the method for preparing metallic lithium according to the present invention, it is possible to directly prepare metallic lithium by electrolysis at a low temperature, and enable mass production, and reduce the manufacturing cost due to its simple process and easy control of electrolytic conditions, and thus the method for preparing lithium thin films according to the present invention can be applied in the industry.

What is claimed is:

1. A method for preparing metallic lithium, the method comprising the steps of:

(a) placing an electrolytic cell including conductive electrodes in a non-aqueous conductive solvent with a dissolved lithium salt in a high purity inert gas atmosphere; and

(b) applying an electric power to the electrolytic cell in step (a) such that lithium is reduced at a cathode and metallic lithium is deposited on the surface of the cathode.

2. The method of claim 1, wherein in step (a), the electrodes comprise at least two metals selected from the group consisting of gold, platinum, and copper.

3. The method of claim 1, wherein in step (a), the inert gas comprises at least one selected from the group consisting of nitrogen, helium, argon, neon, and xenon.

4. The method of claim 1, wherein in step (a), the lithium salt comprises at least one selected from the group consisting of LiTFSI, LiCl, LiF, LiPF<sub>6</sub>, and LiBF<sub>4</sub>.

5. The method of claim 1, wherein in step (a), the non-aqueous conductive solvent is a non-aqueous conductive solvent containing a bis(trifluoromethylsulfonyl)imide (TFSI) anion and comprises at least one selected from the group consisting of 1-Butyl-3-methyl-pyridinium bis(trifluoromethylsulfonyl)imide ([BMPy]TFSI), 1-methyl-propylpiperidinium bis(trifluoromethylsulfonyl)imide (PP13TFSI), and 1-Ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide ([EMIM]TFSI).

6. The method of claim 5, wherein the non-aqueous conductive solvent further comprises propylene carbonate (PC), dichloromethane (DCM), tetrahydrofuran (THF), dicyanamide (DCA), or N-methylpyrrolidone (NMP).

7. The method of claim 1, further comprising, before step (a), the steps of:

(a') washing the electrodes and the cell with a mixed solution of sulfuric acid and hydrogen peroxide; and

(a'') drying the non-aqueous solvent at 80 to 120° C. for 20 to 30 hours.

8. The method of claim 1, wherein in step (b), the reduction of lithium is performed by pulsed plating such that the lithium is deposited.

9. The method of claim 1, further comprising, after step (b), the step of performing heat treatment on the deposited lithium at 800 to 900° C. for 30 to 90 minutes in an inert gas atmosphere.

10. The method of claim 9, wherein the inert gas comprises at least one selected from the group consisting of nitrogen, helium, argon, neon, and xenon.

11. A metallic lithium prepared by the method of claim 1.

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