

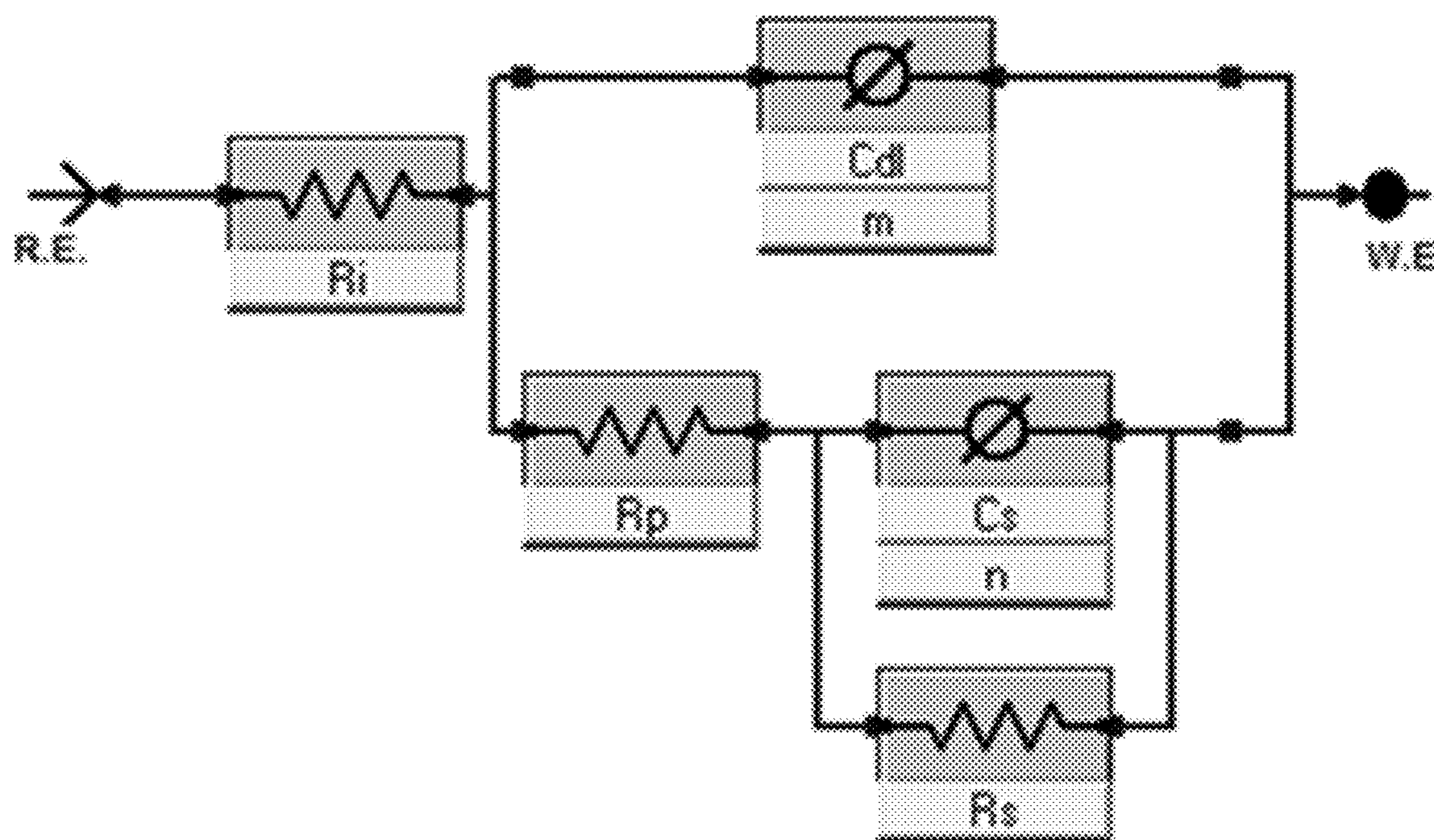
US 20160289849A1

(19) **United States**(12) **Patent Application Publication**  
**Sun et al.**(10) **Pub. No.: US 2016/0289849 A1**(43) **Pub. Date: Oct. 6, 2016**(54) **BIFUNCTIONAL WATER SPLITTING  
CATALYSTS AND ASSOCIATED METHODS**(71) Applicants: **Yujie Sun**, North Logan, UT (US); **Nan Jiang**, Logan, UT (US); **Bo You**, Logan, UT (US)(72) Inventors: **Yujie Sun**, North Logan, UT (US); **Nan Jiang**, Logan, UT (US); **Bo You**, Logan, UT (US)(21) Appl. No.: **15/087,999**(22) Filed: **Mar. 31, 2016****Related U.S. Application Data**

(60) Provisional application No. 62/141,081, filed on Mar. 31, 2015.

**Publication Classification**(51) **Int. Cl.**  
**C25B 1/04** (2006.01)**C25D 13/02** (2006.01)(52) **U.S. Cl.**  
CPC ..... **C25B 1/04** (2013.01); **C25D 13/02** (2013.01)(57) **ABSTRACT**

A catalyst, including a conductive substrate coated with a metal-phosphorus-derived film, where the metal is Manganese, Iron, Cobalt, Nickel, or Copper. In some embodiments, the conductive substrate includes copper, titanium, glassy carbon, fluorine-doped tin oxide, indium-doped tin oxide, tin, nickel, or stainless steel. Methods for producing the catalysts and for hydrogen evolution reactions and oxygen evolution reactions employing the catalysts are also described herein.



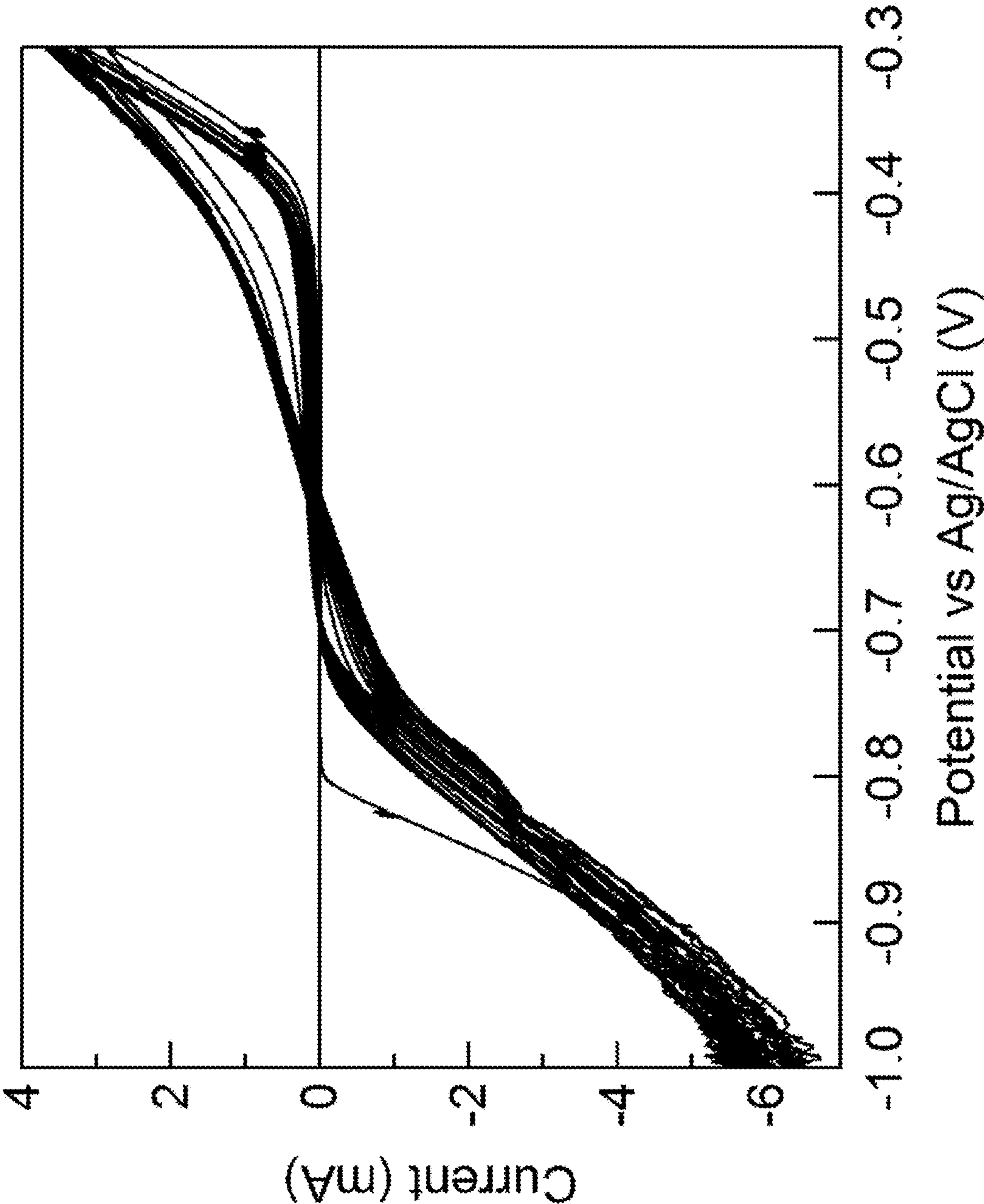


FIG.1

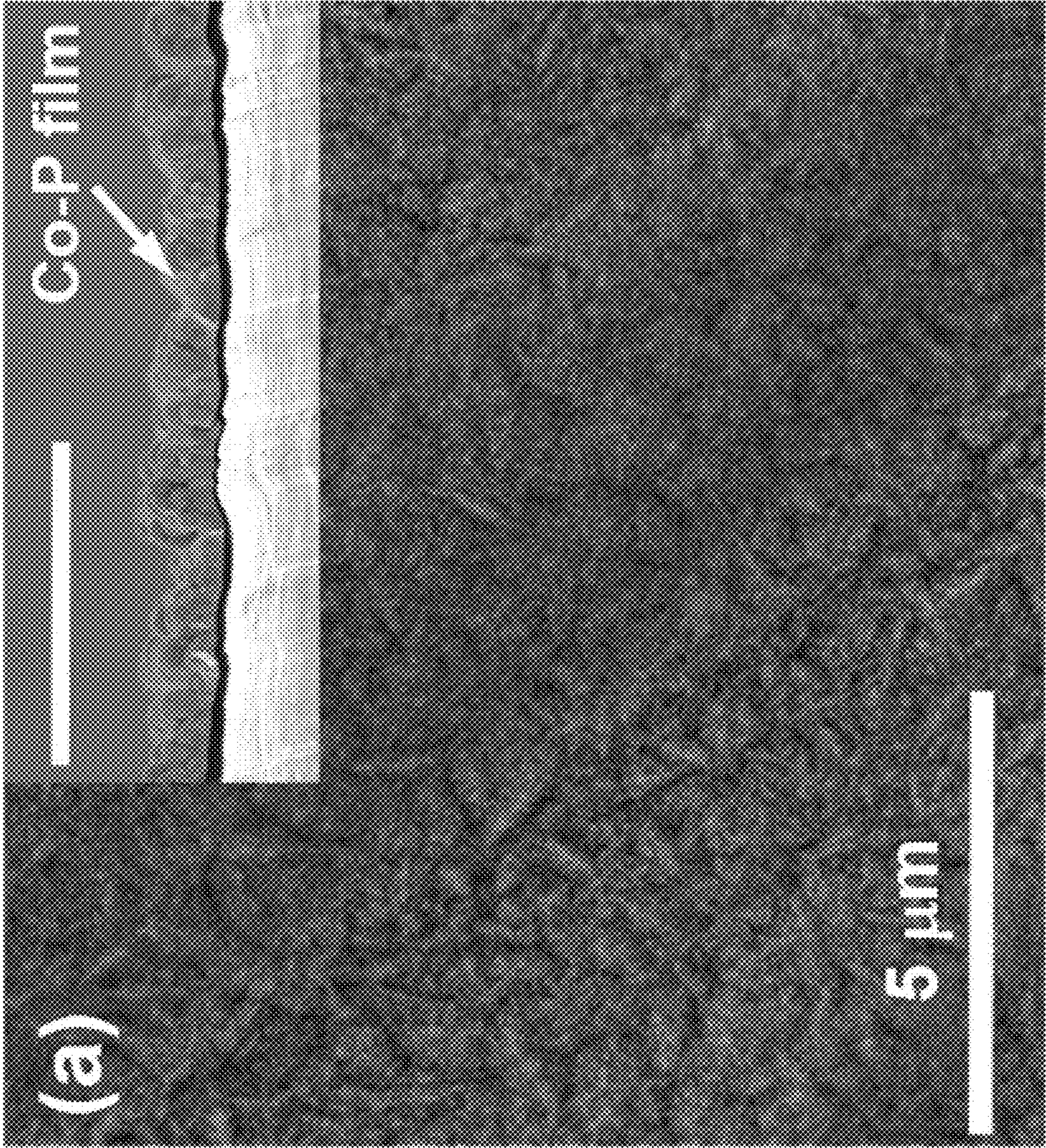


FIG. 2(a)

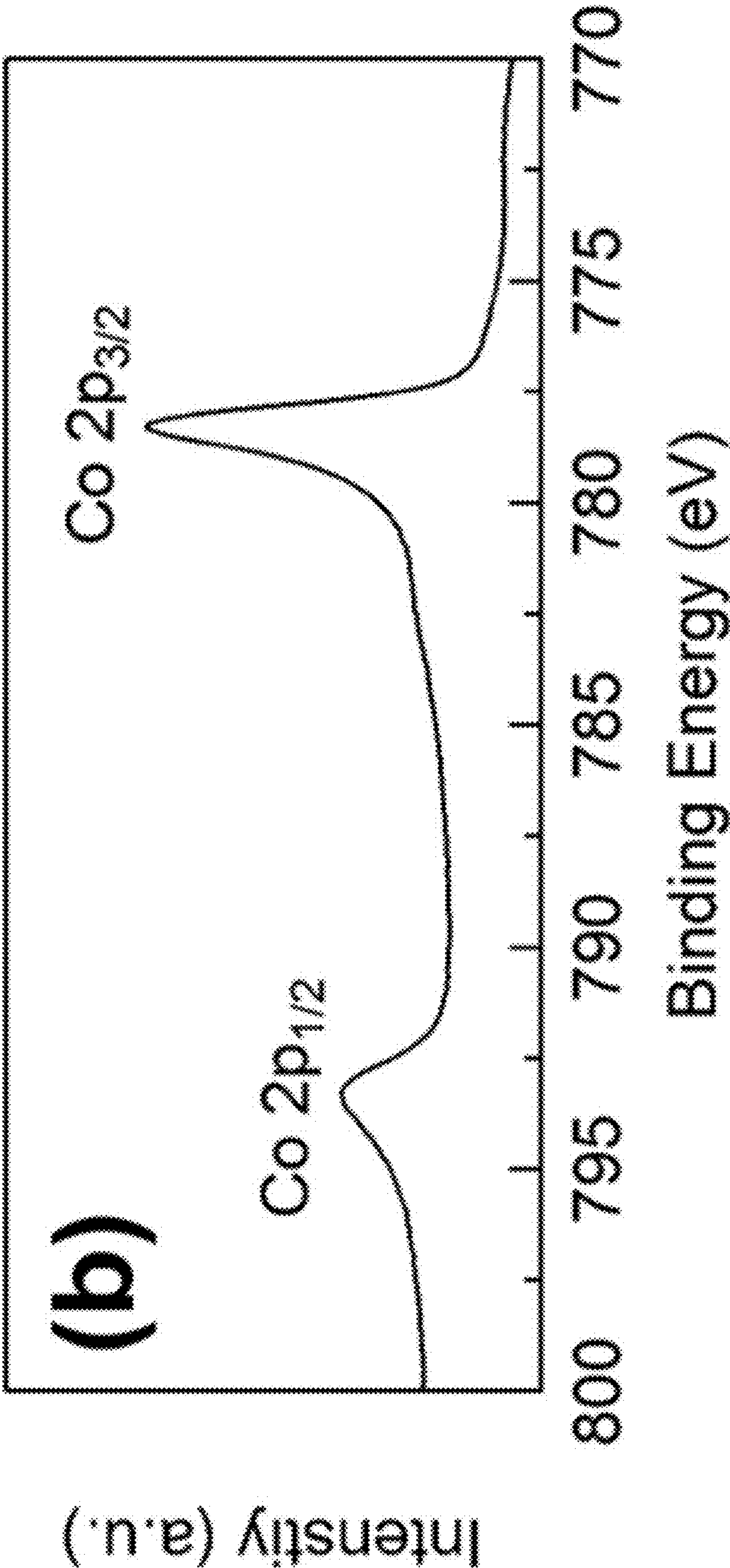


FIG. 2(b)

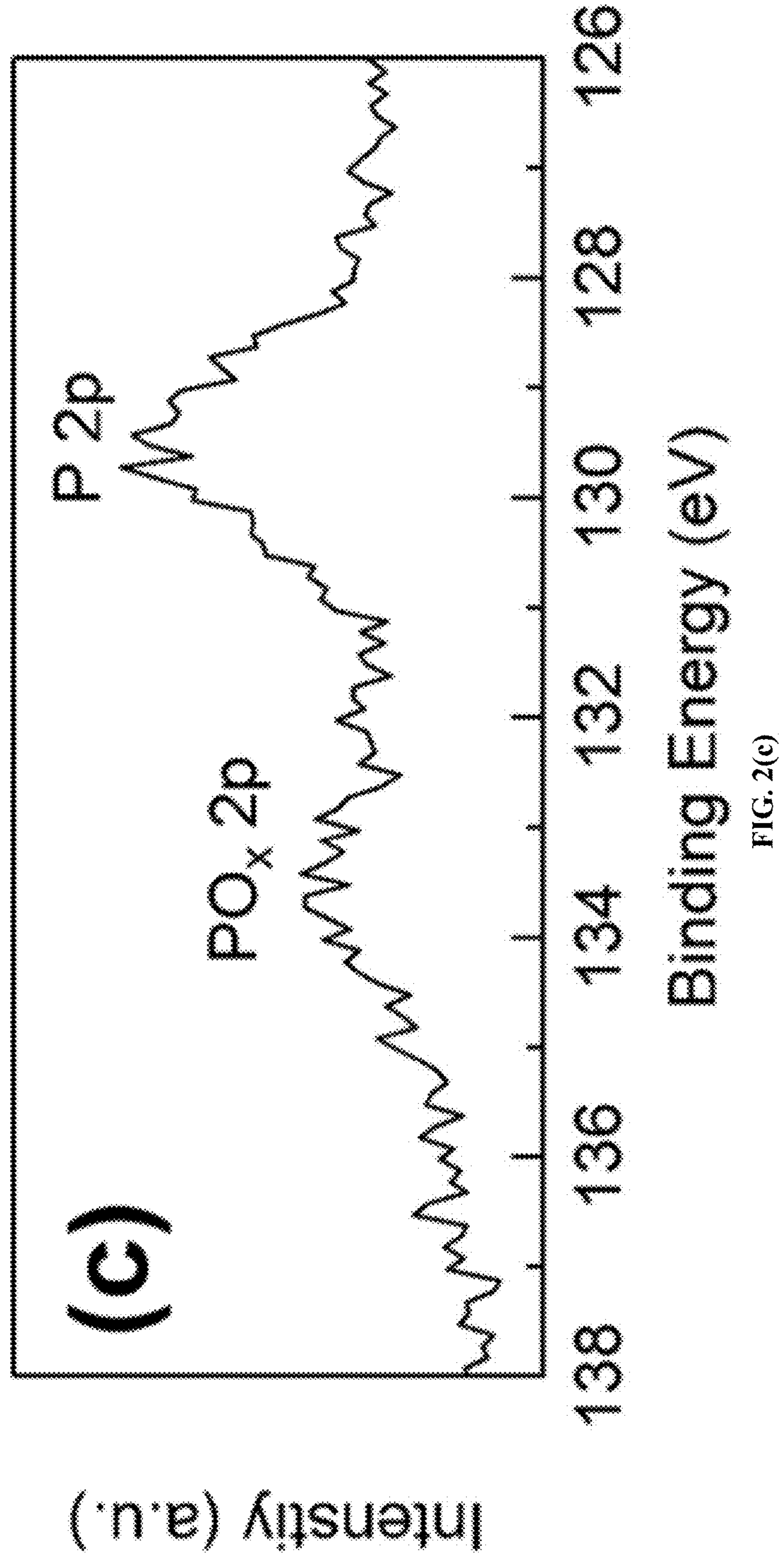


FIG. 2(c)

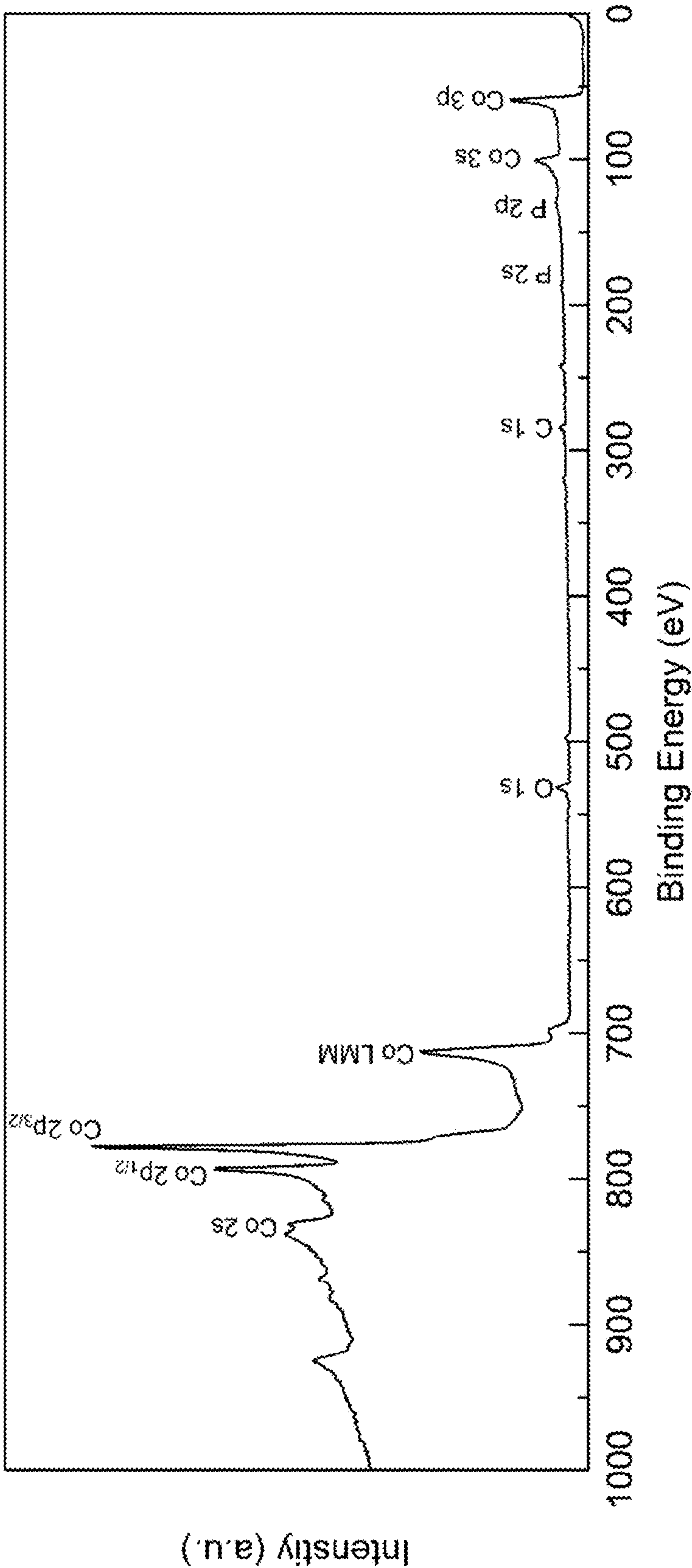


FIG. 3

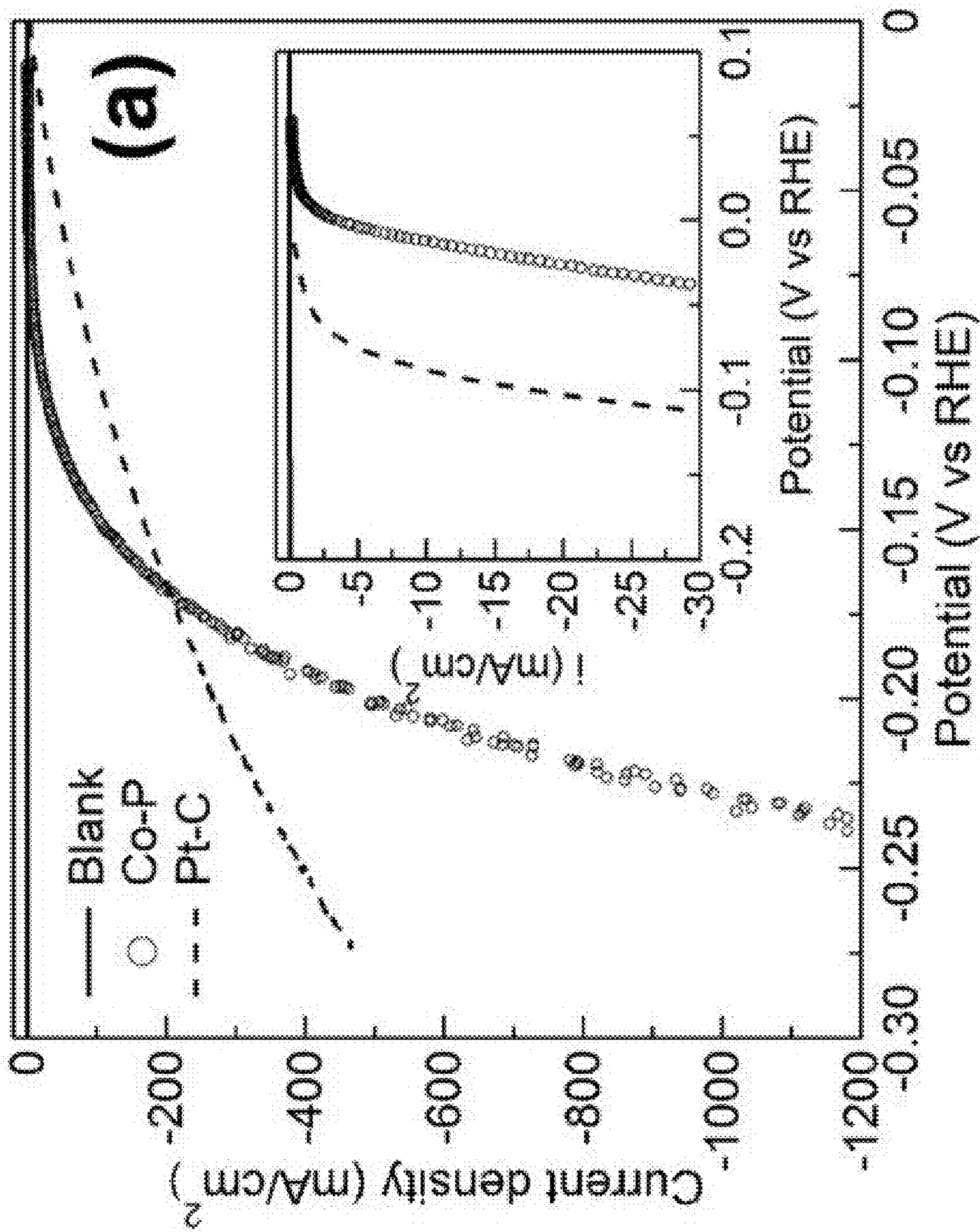


FIG. 4(a)

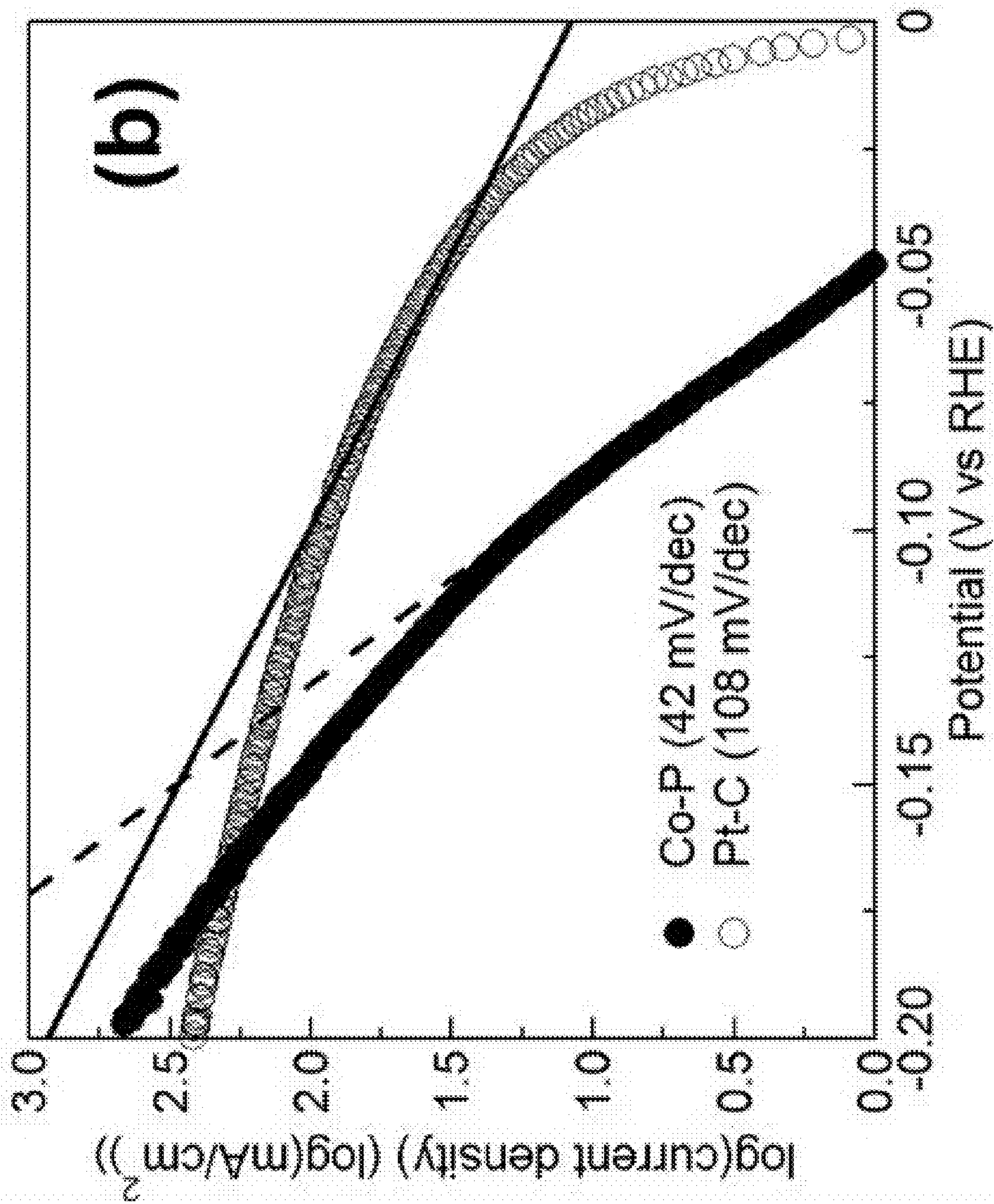


FIG. 4(b)

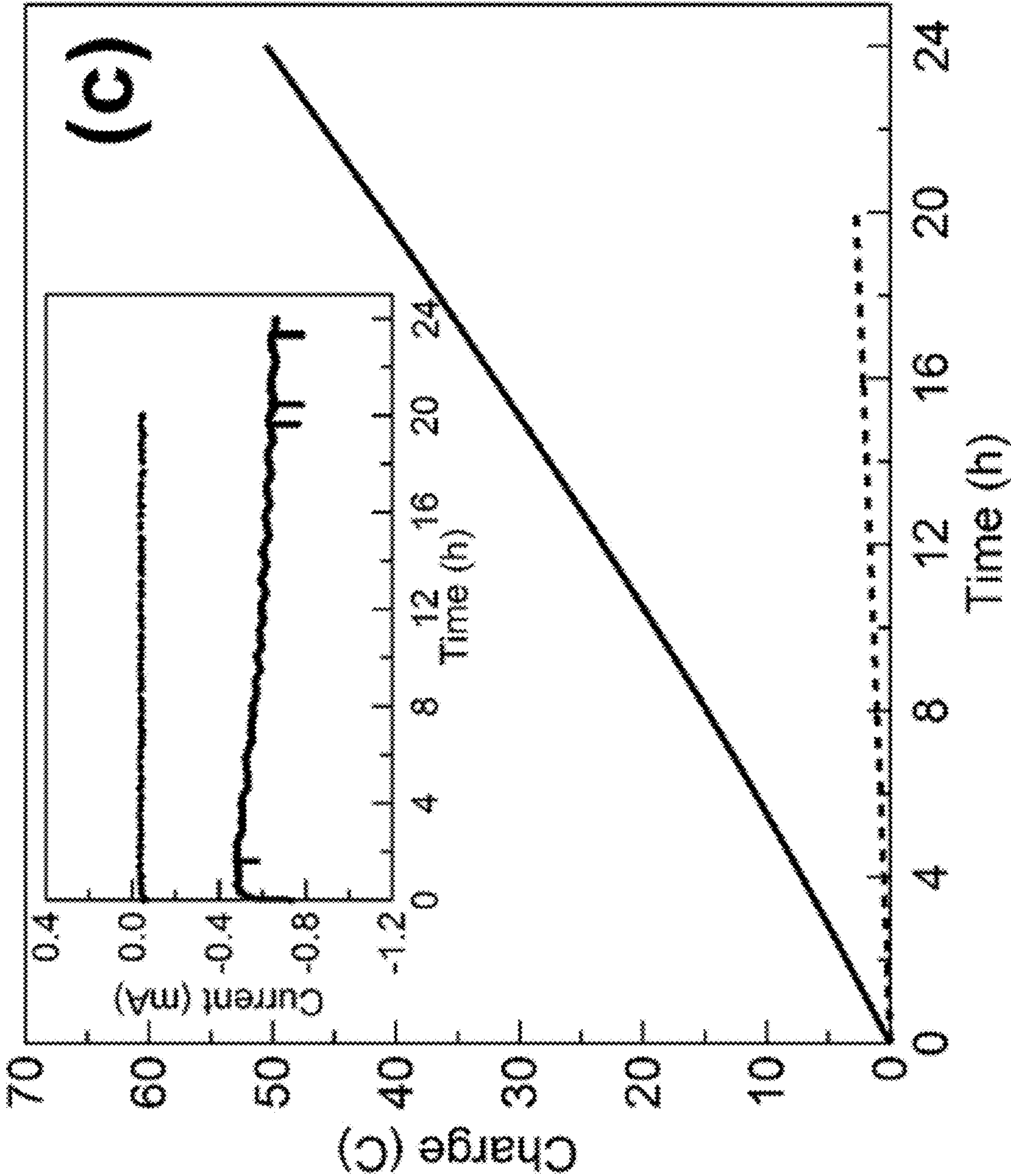


FIG. 4(c)

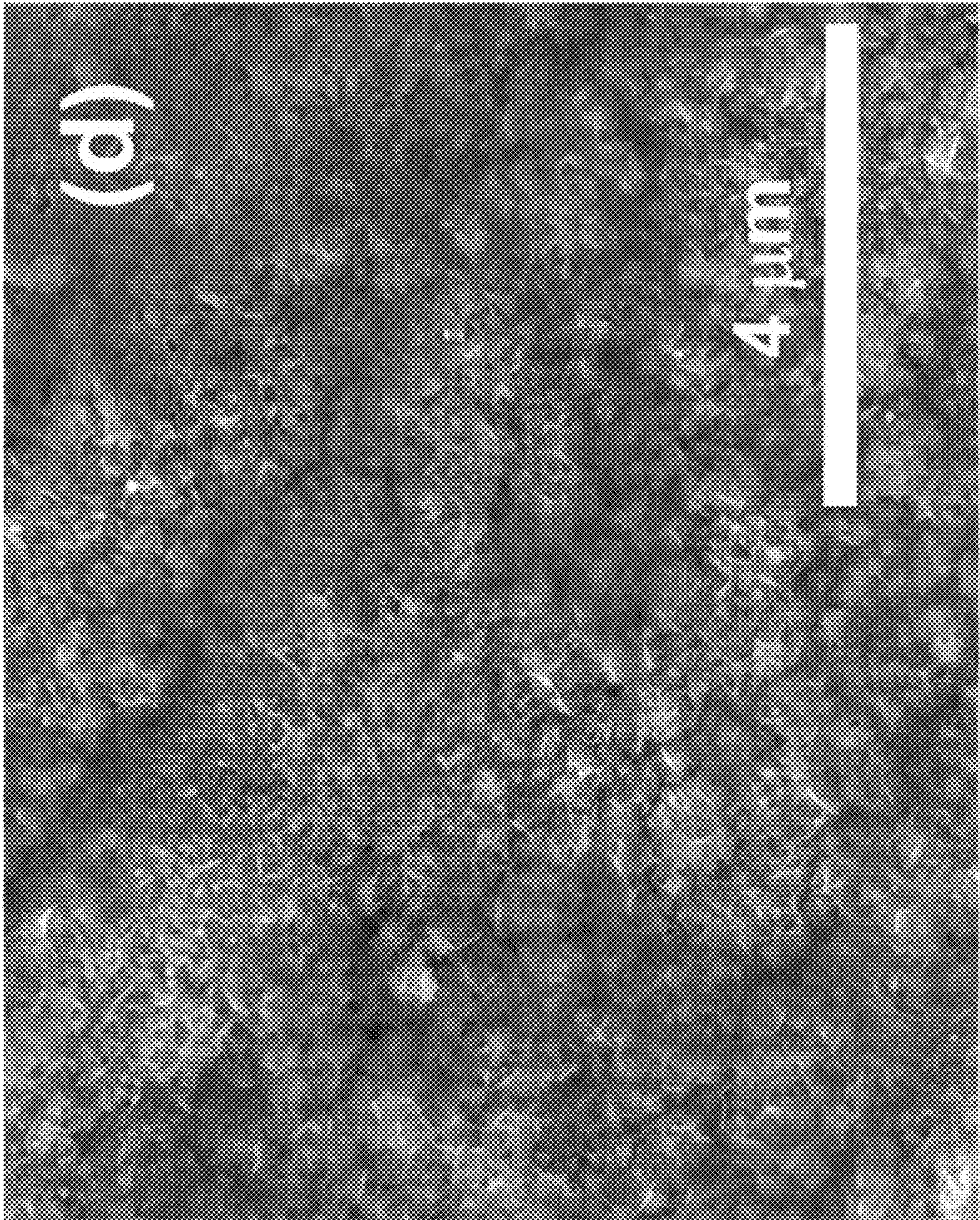


FIG. 4(d)

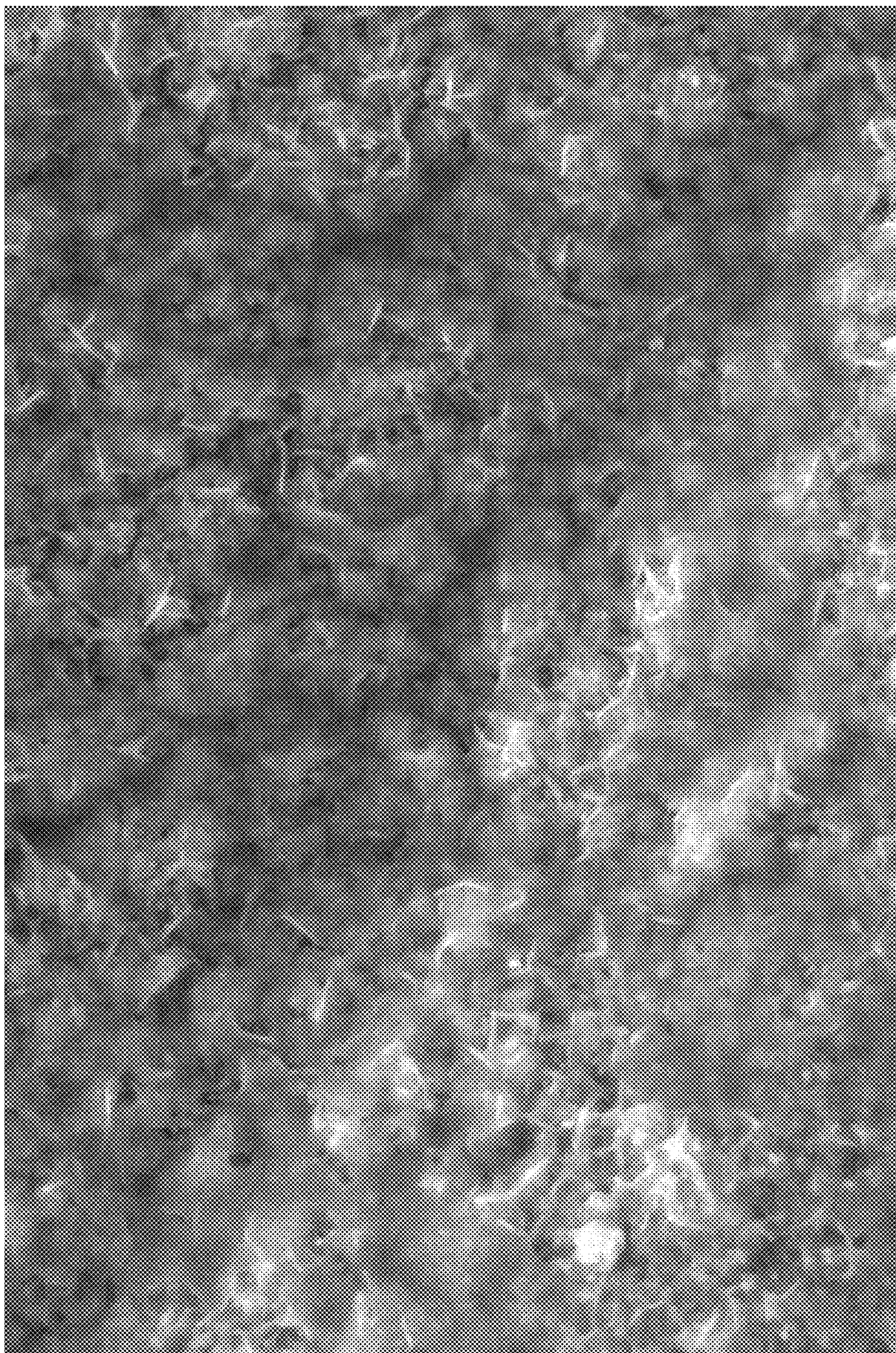


FIG. 5

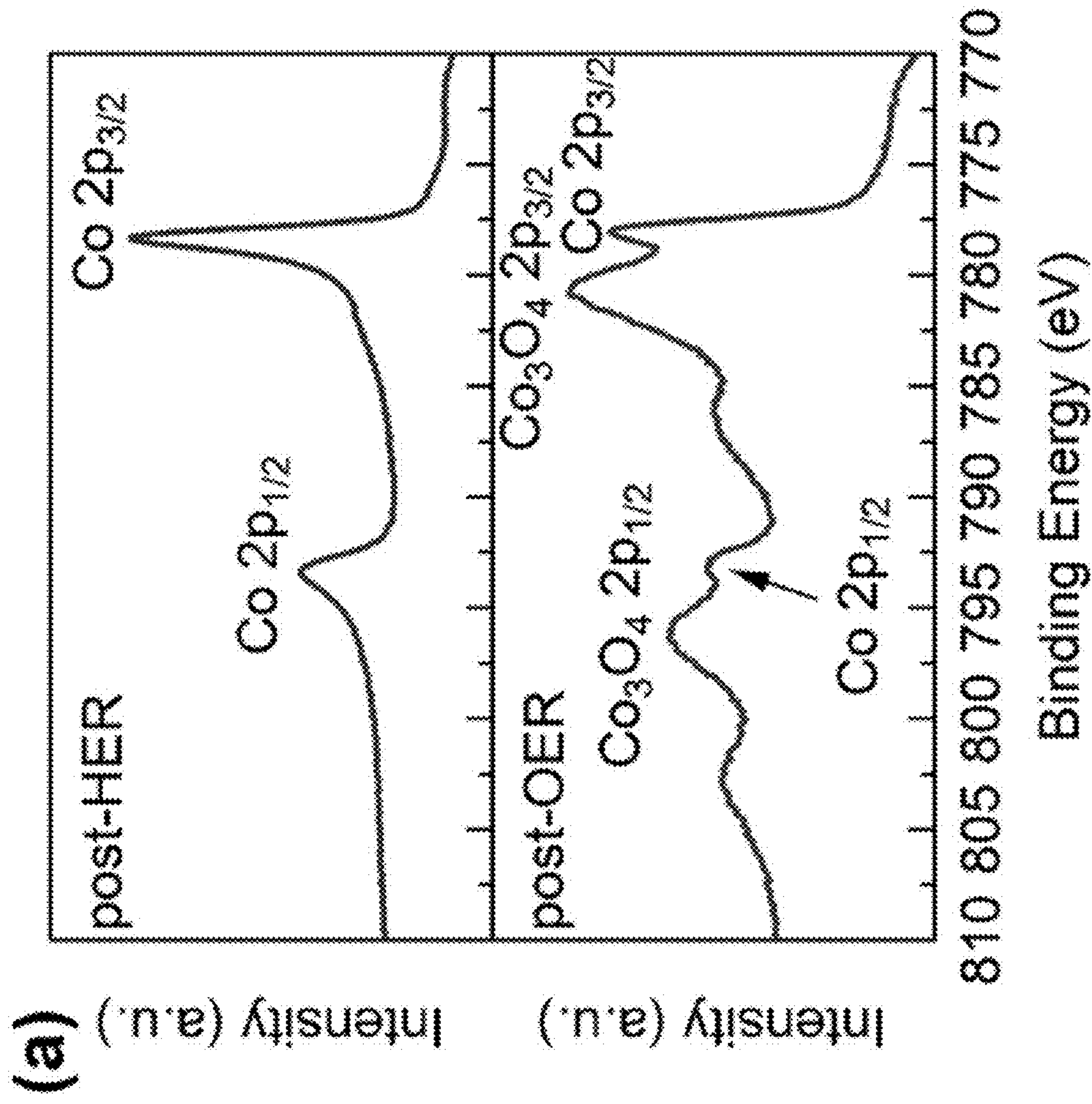


FIG. 6(a)

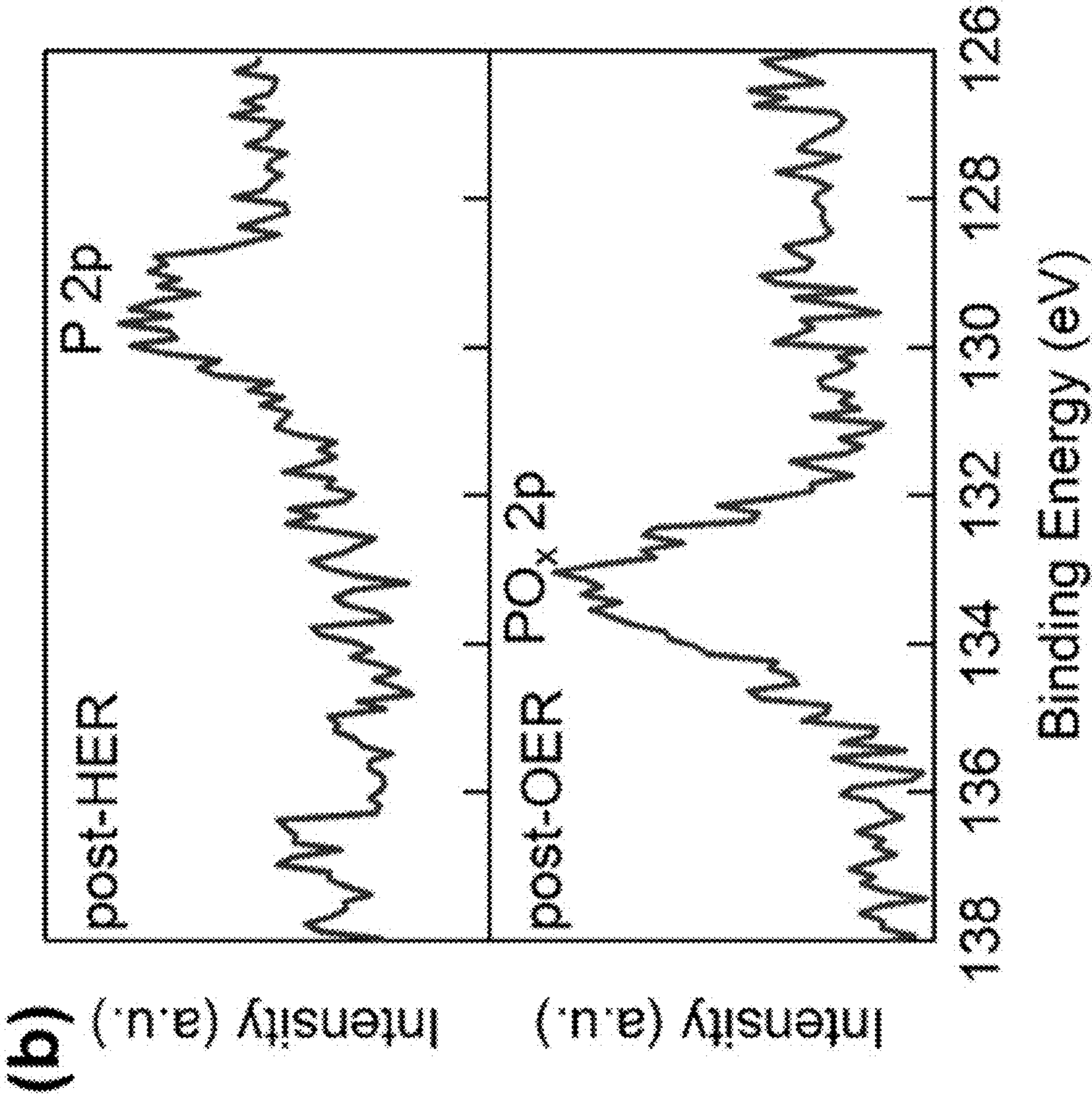


FIG. 6(b)

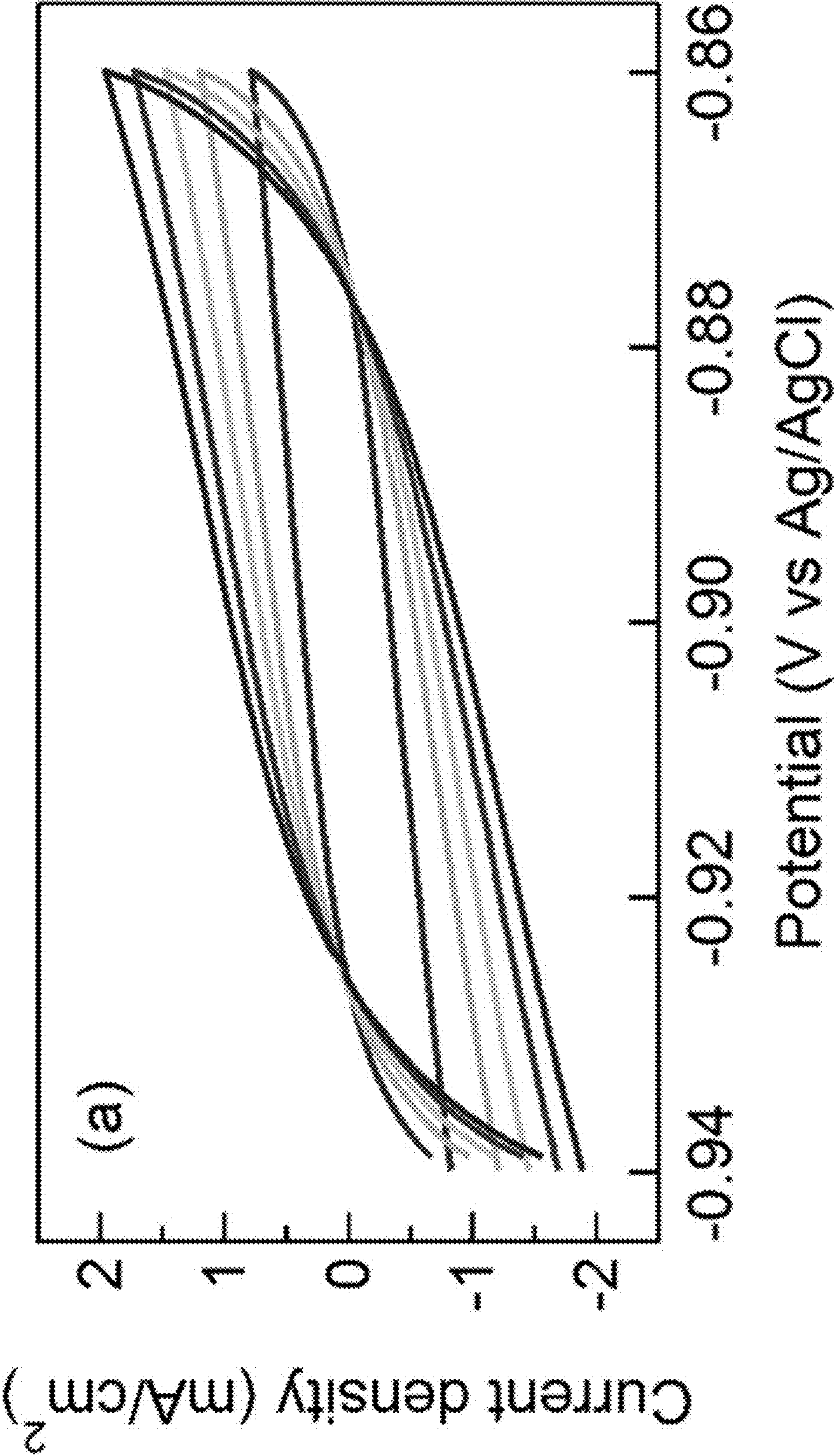


FIG. 7(a)

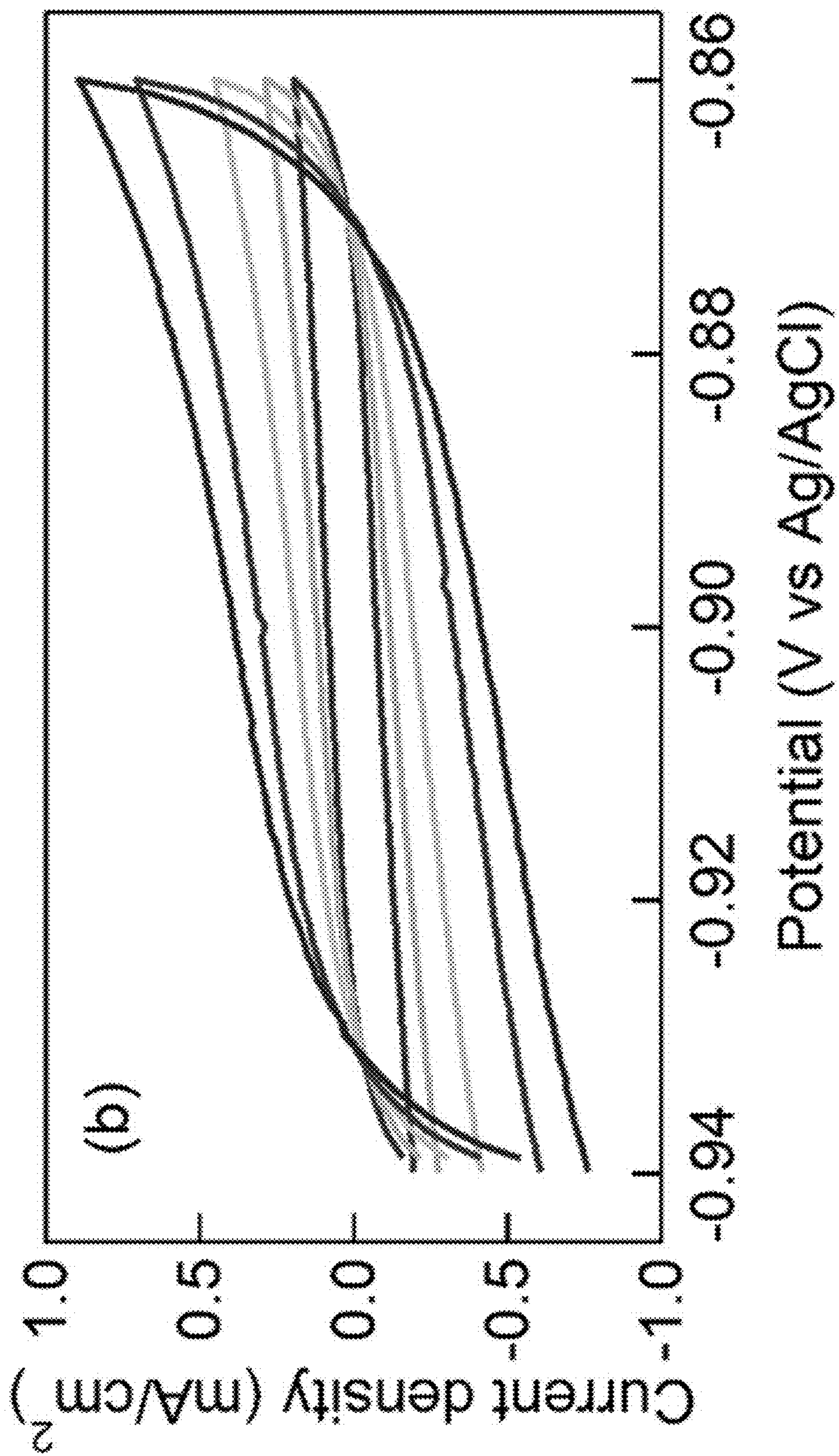


FIG. 7(b)

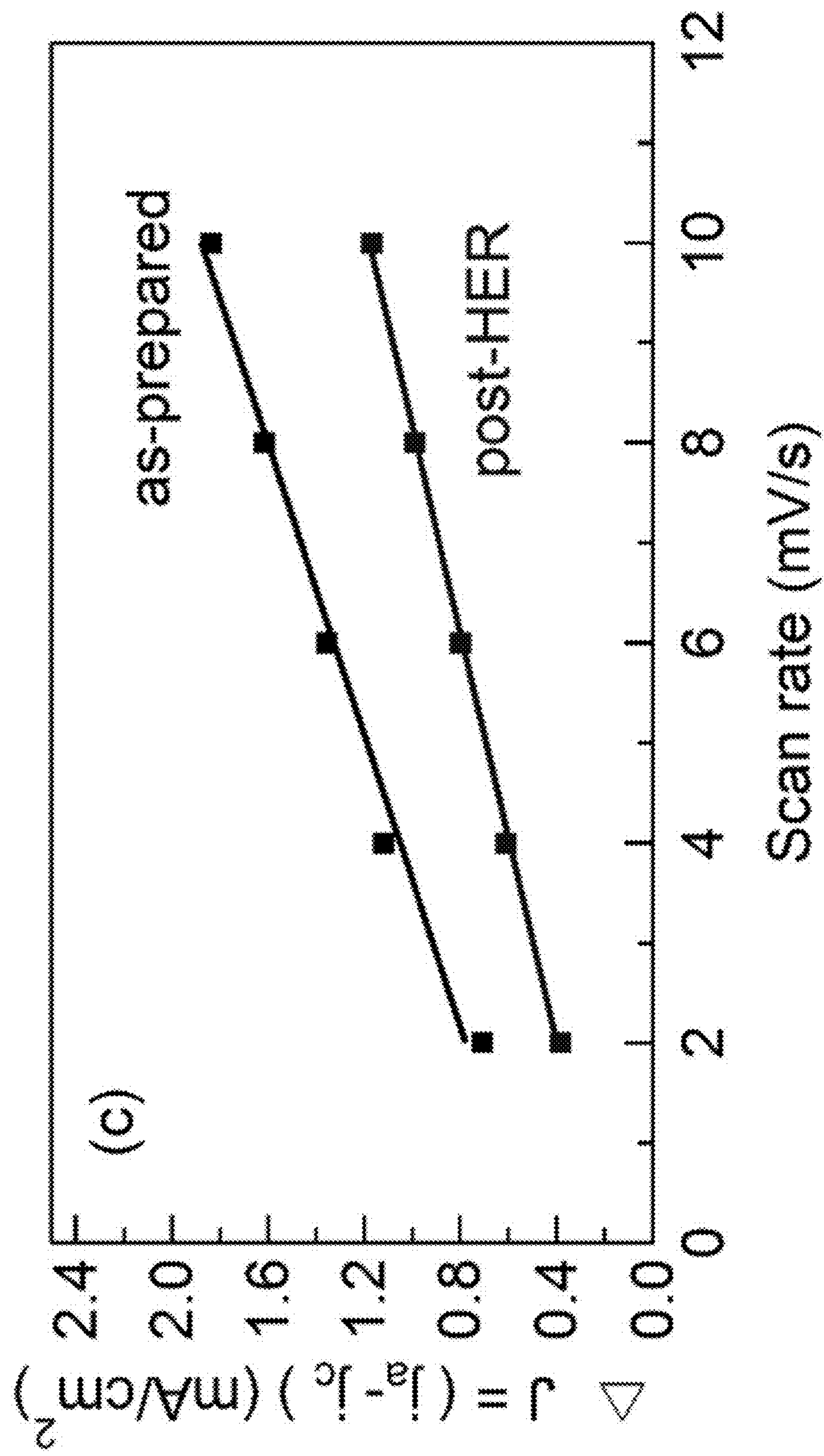


FIG. 7(c)

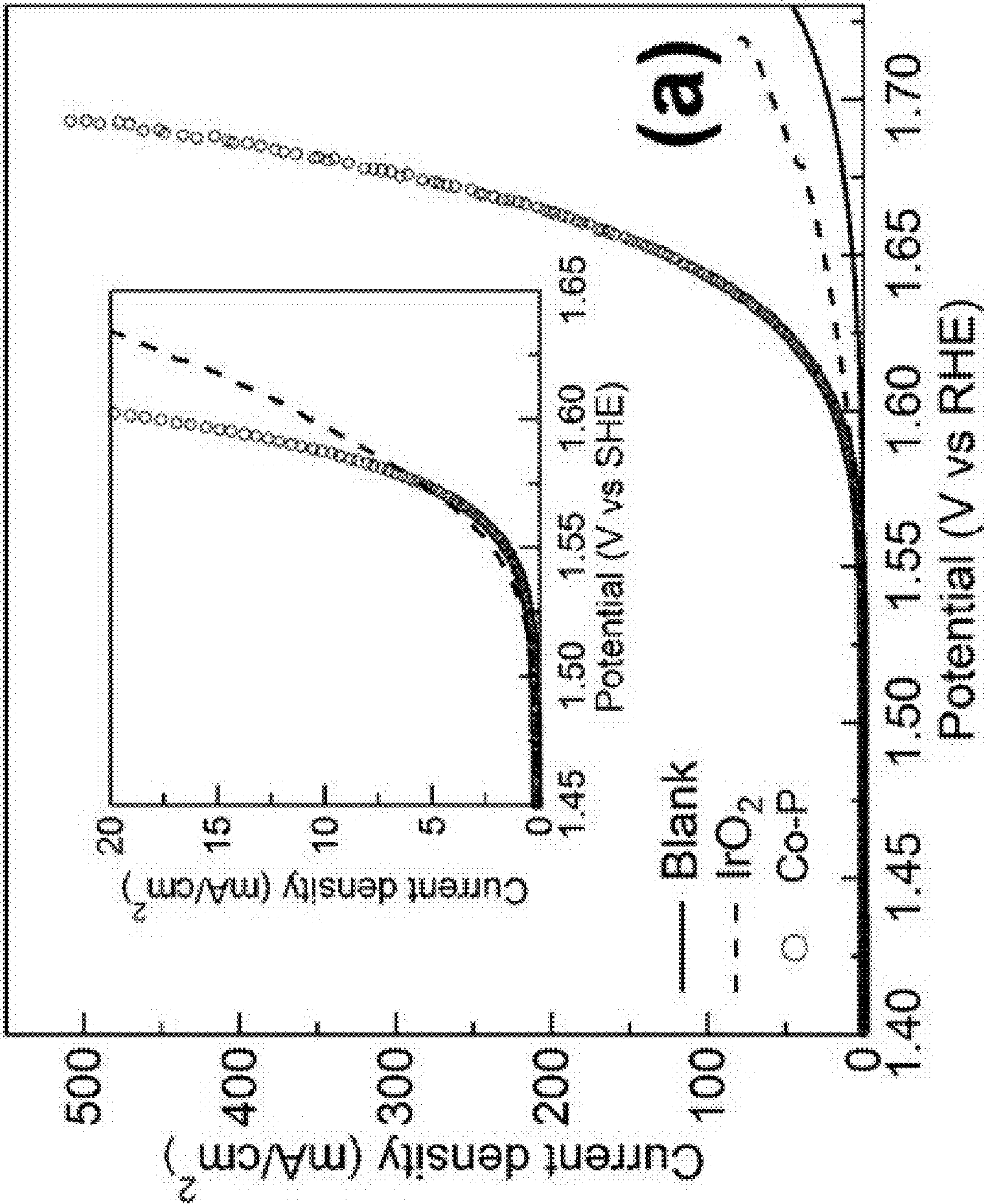


FIG. 8(a)

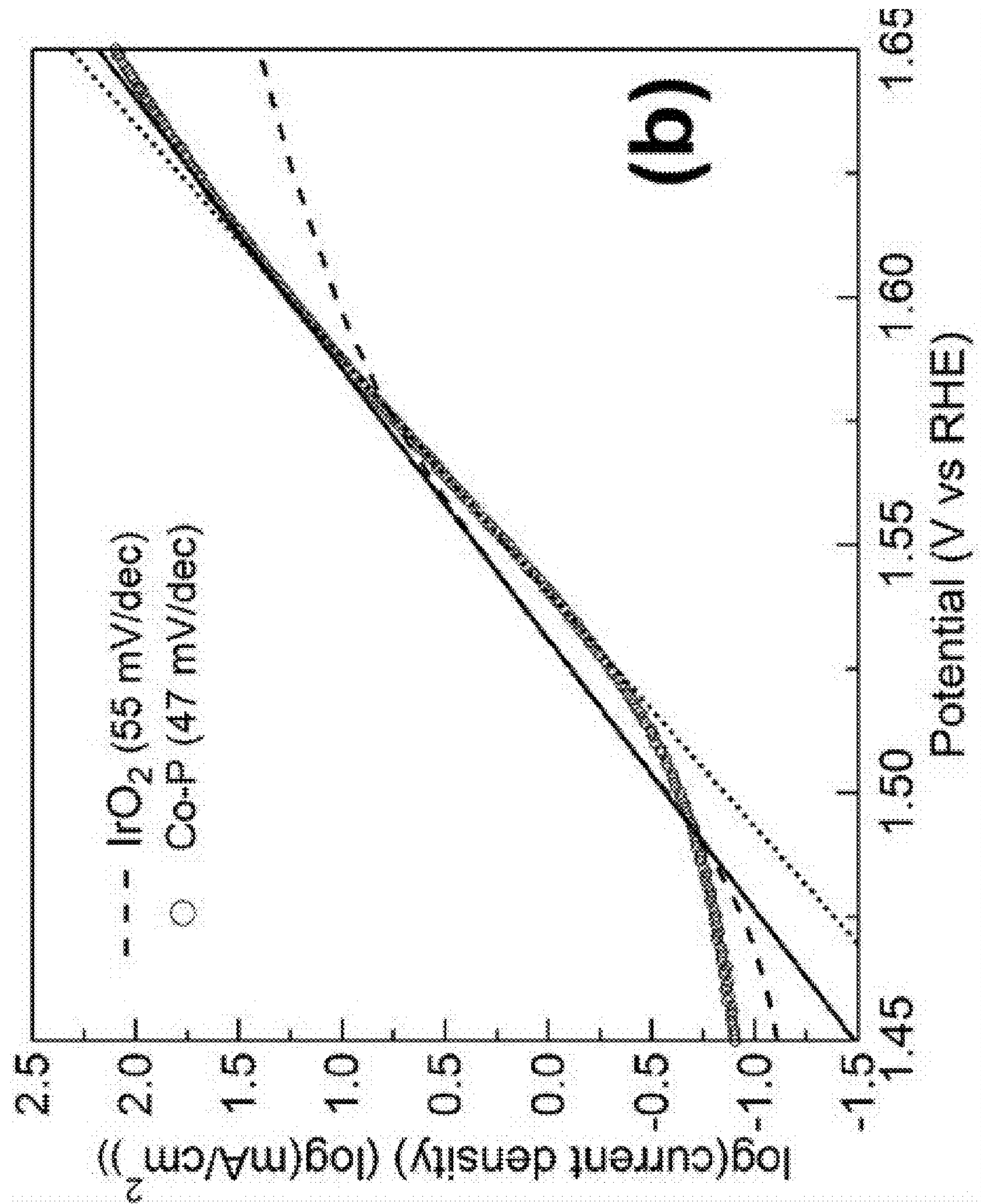


FIG. 8(b)

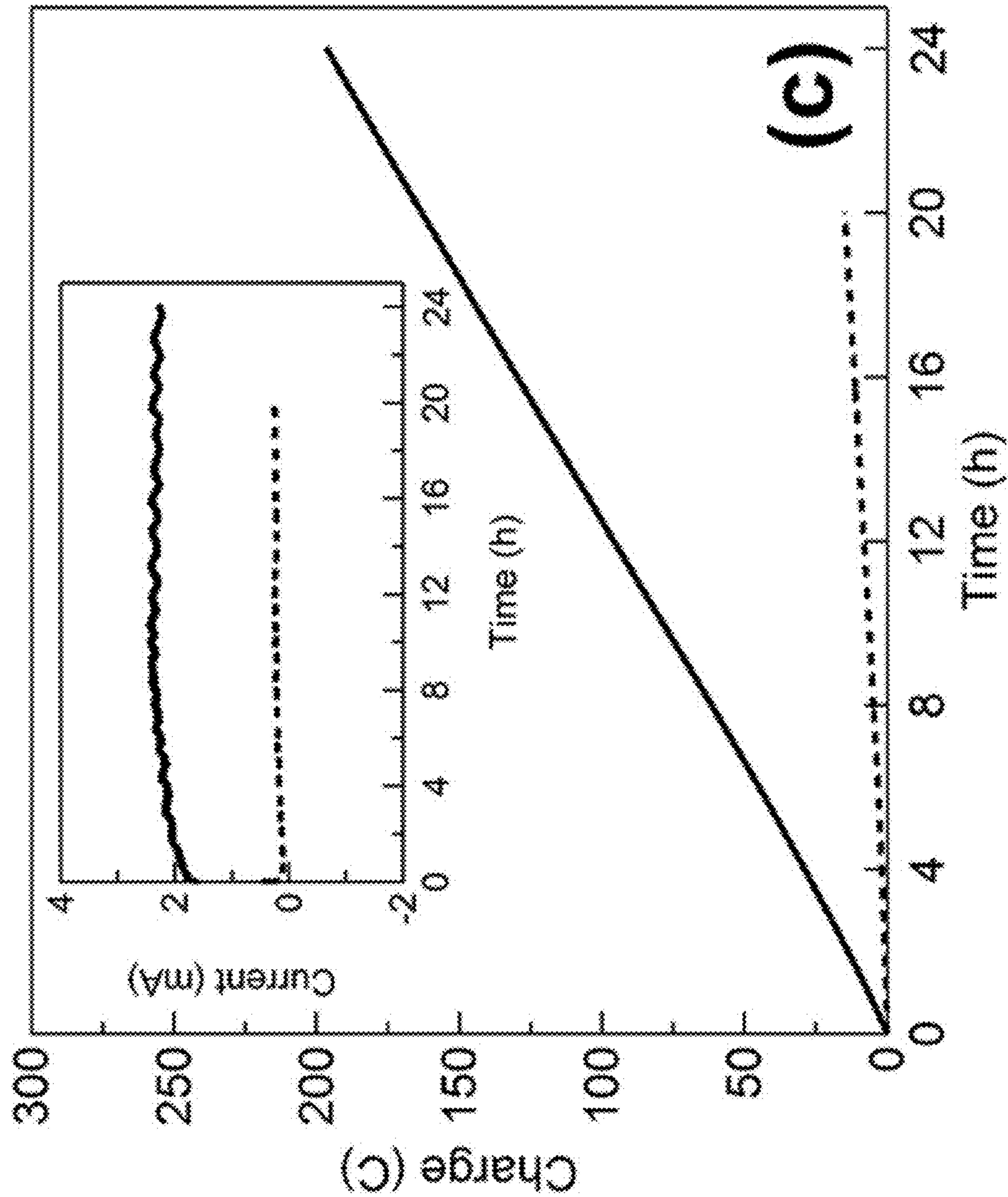


FIG. 8(c)

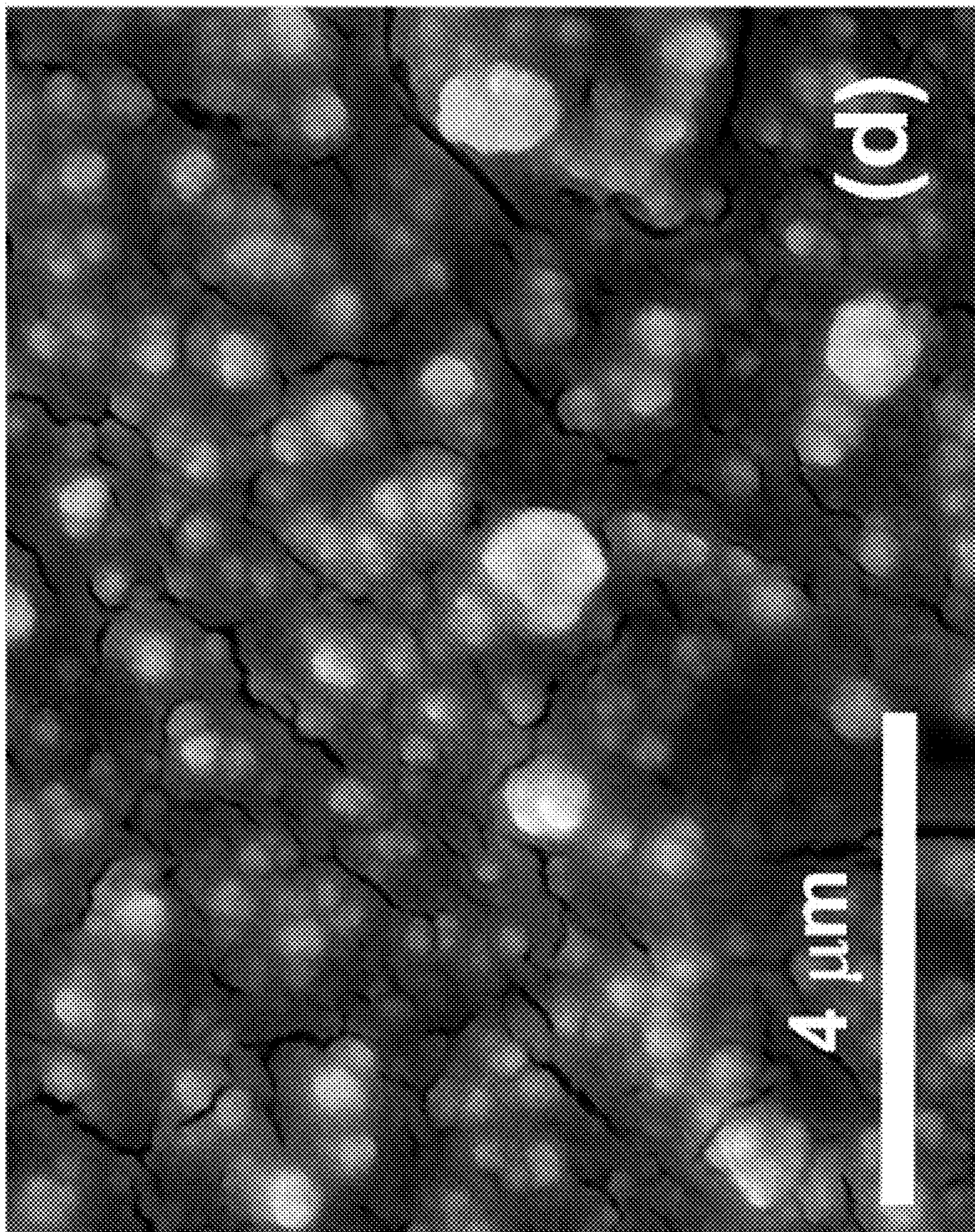


FIG. 8(d)

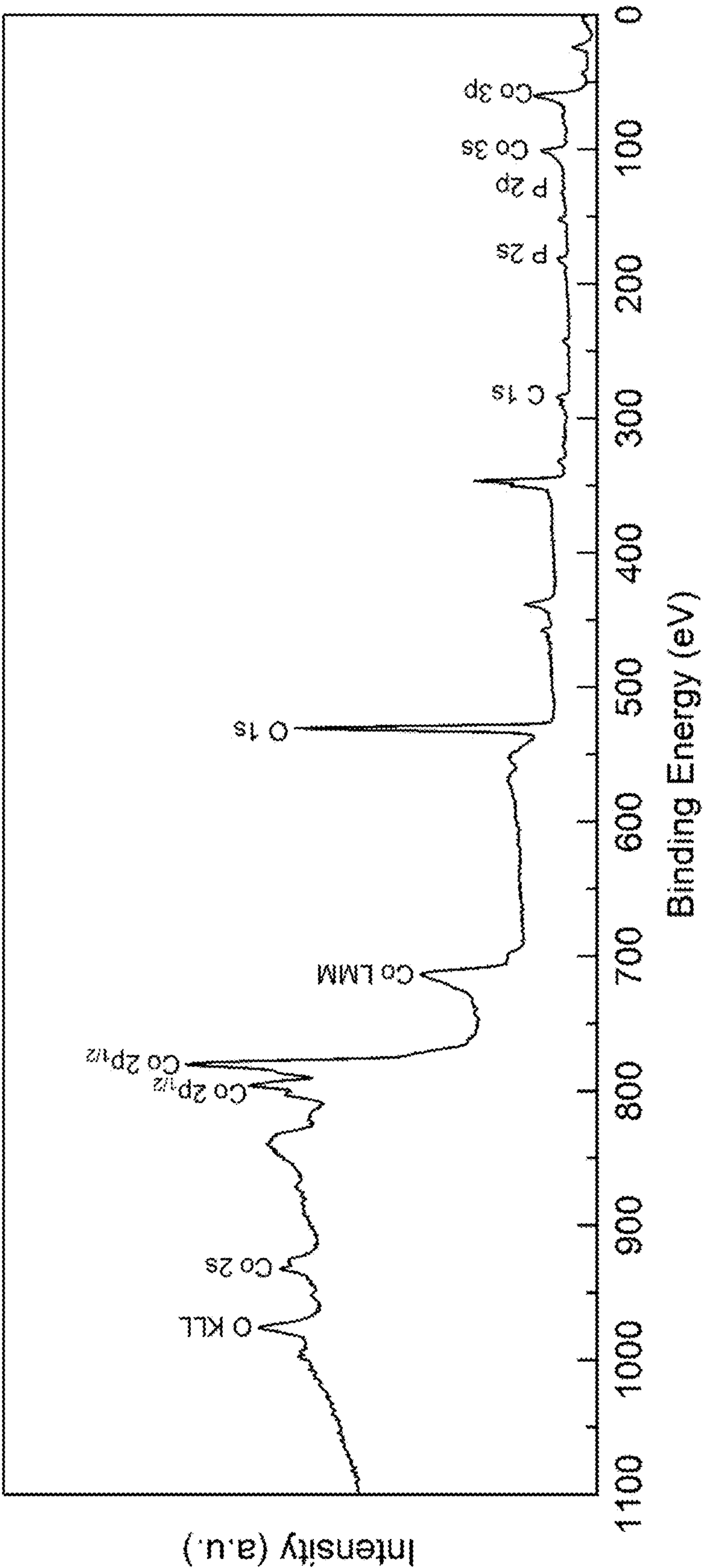


FIG. 9

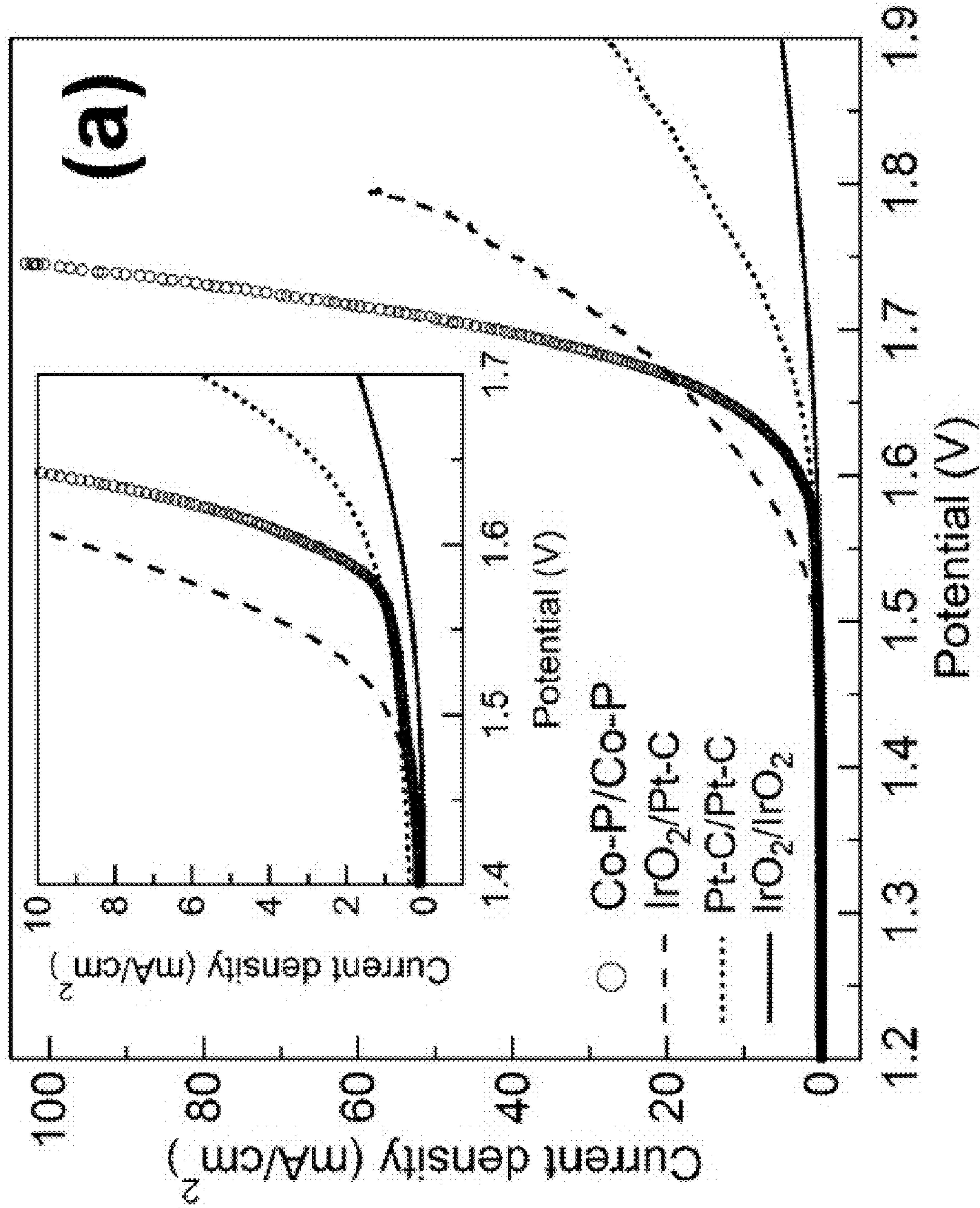


FIG. 10(a)

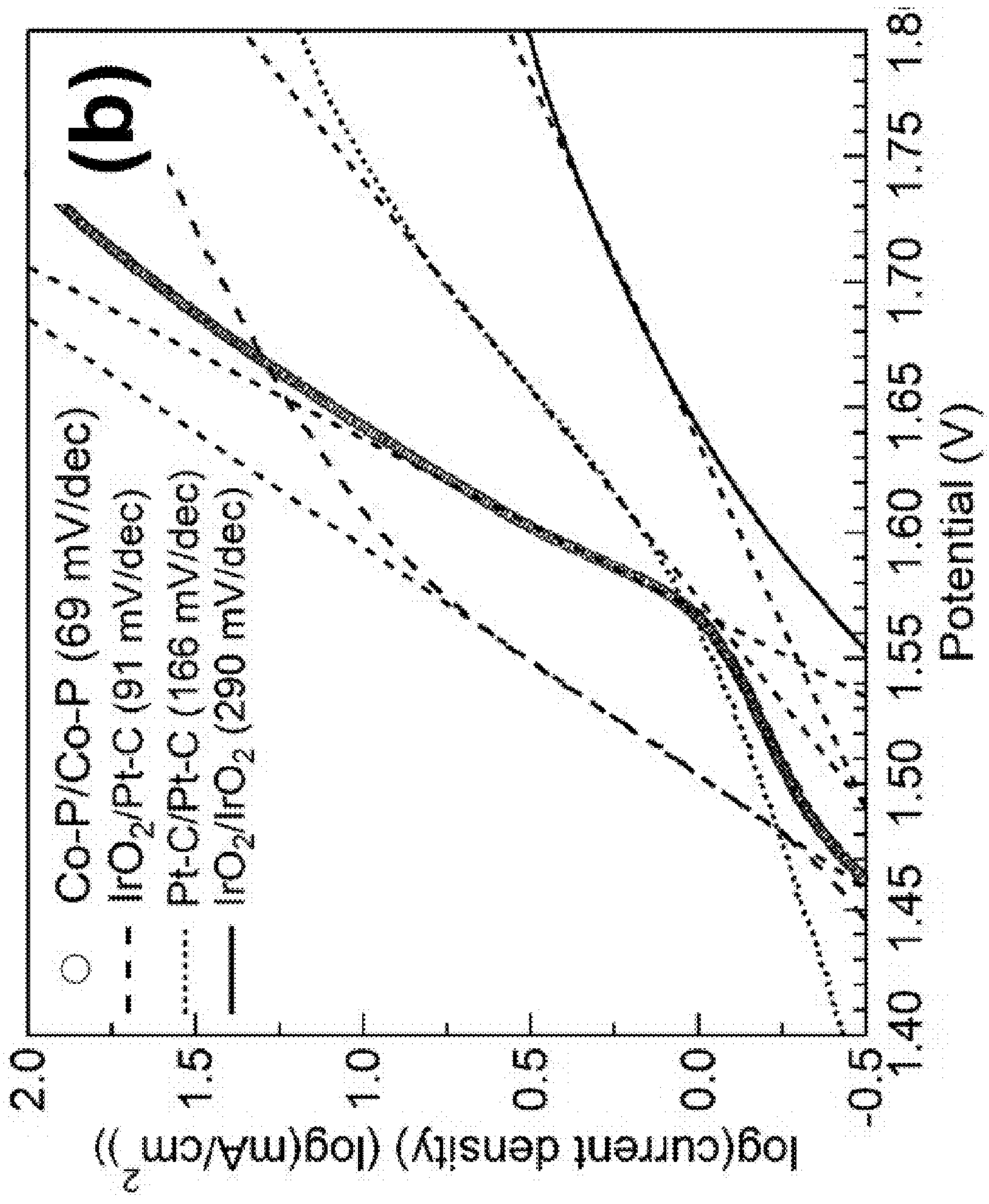


FIG. 10(b)

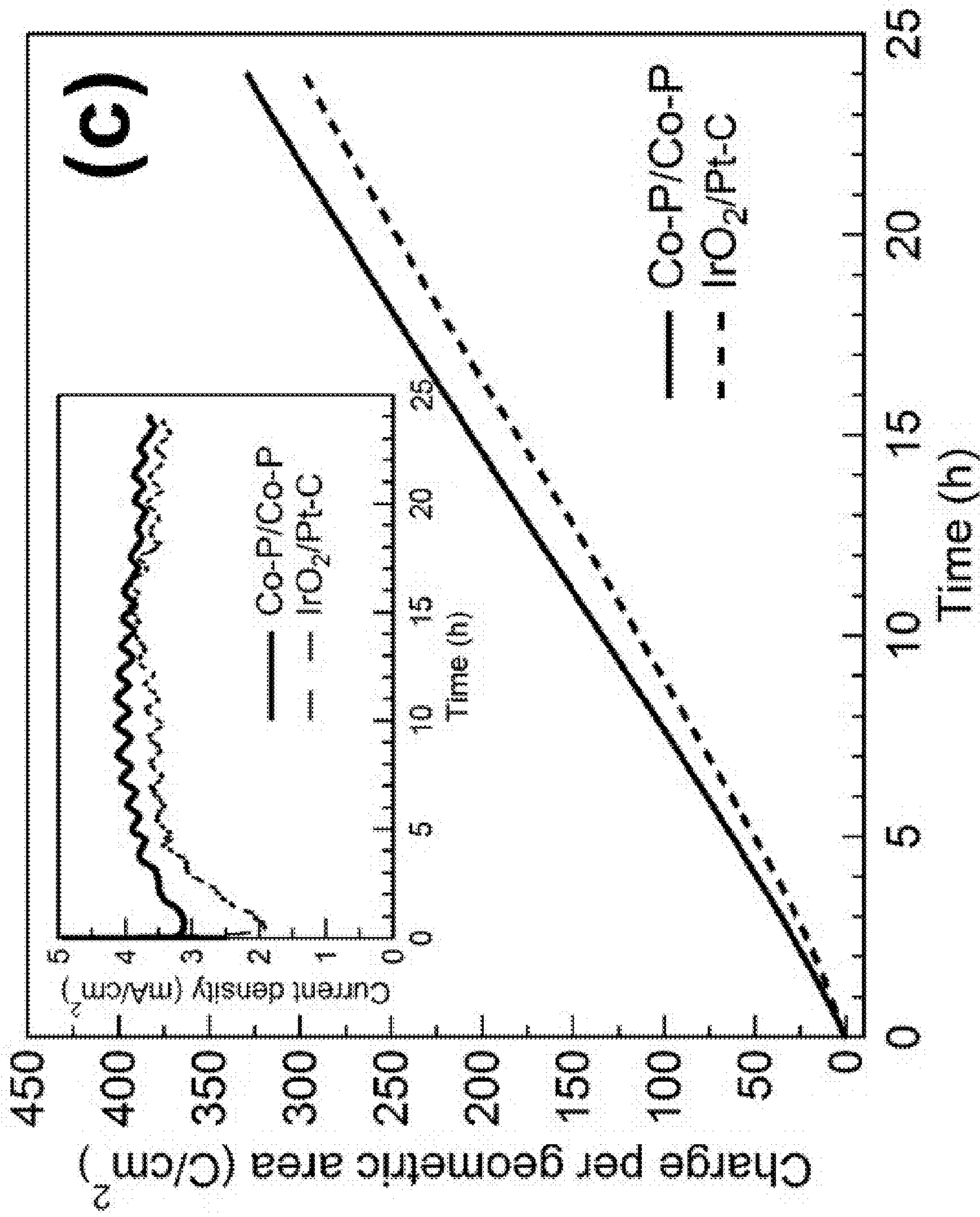


FIG. 10(c)

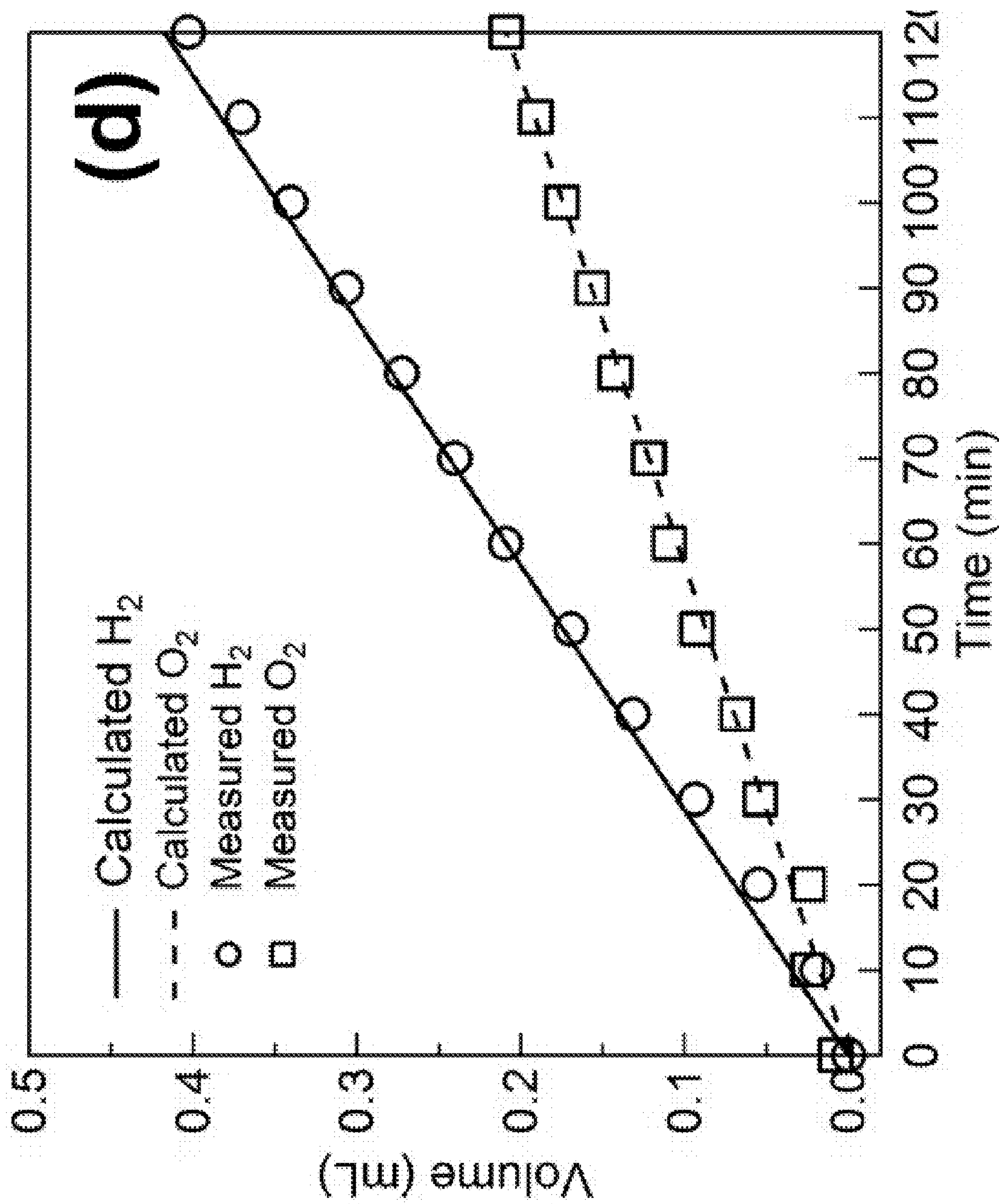


FIG. 10(d)

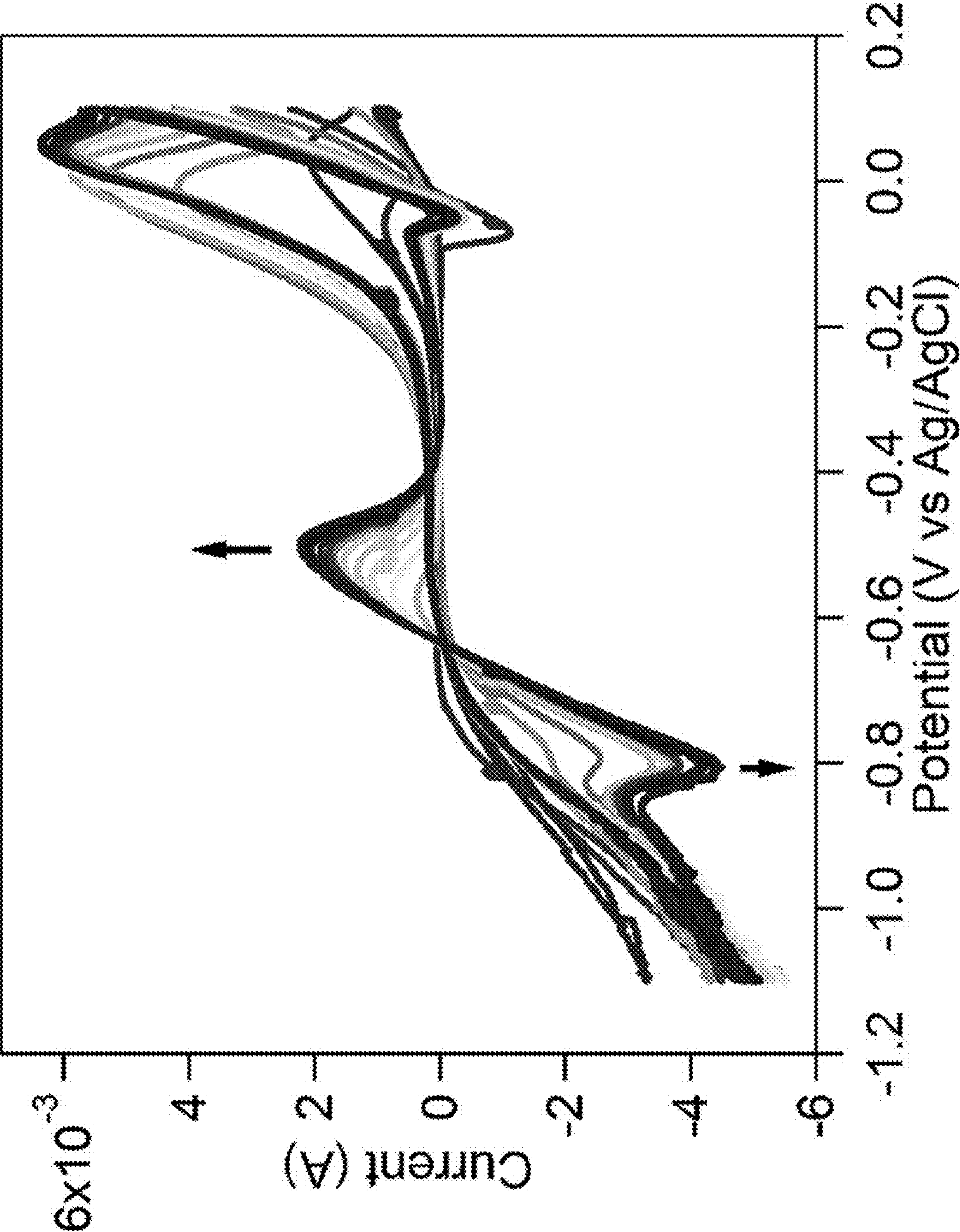


FIG. 11

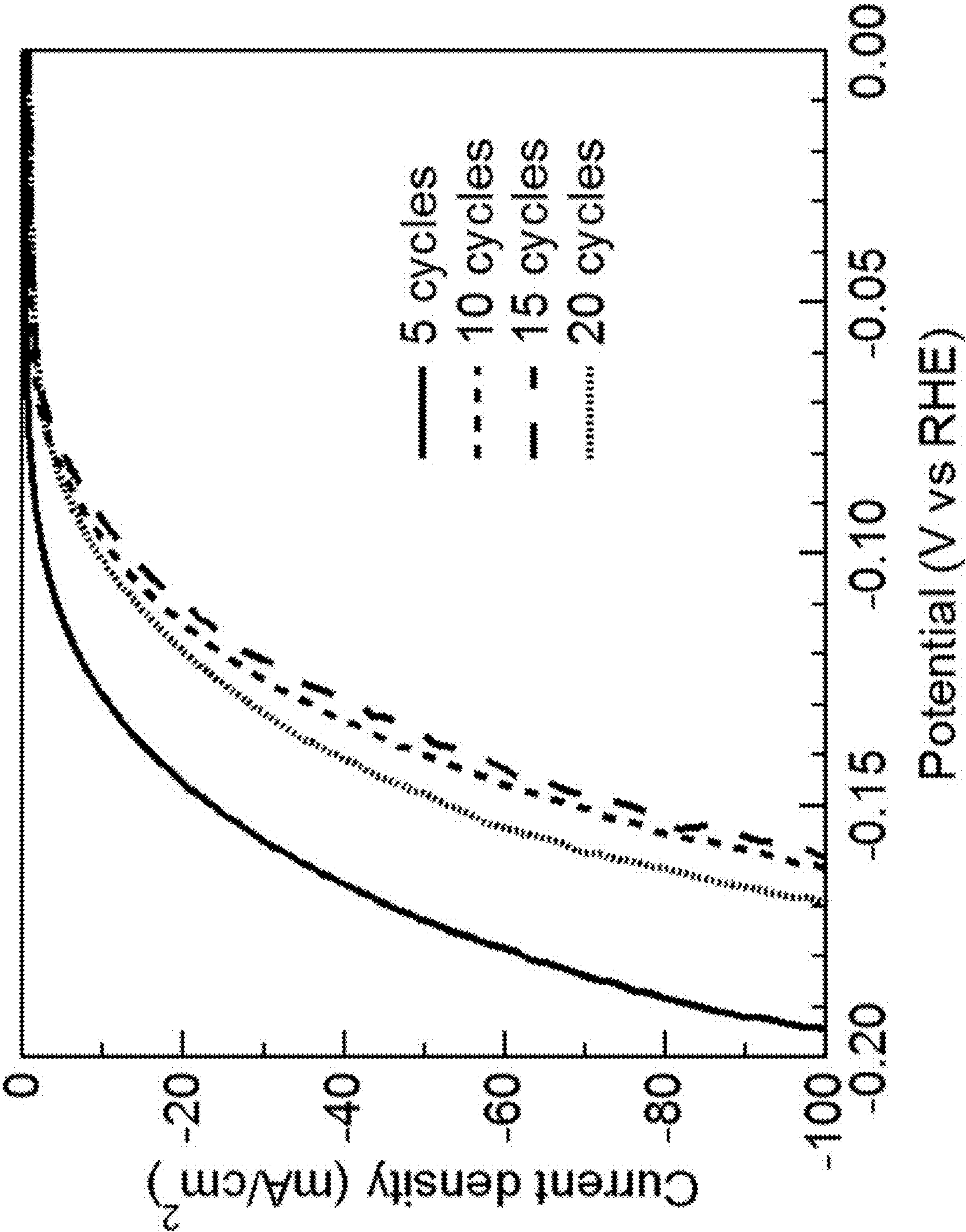


FIG. 12(a)

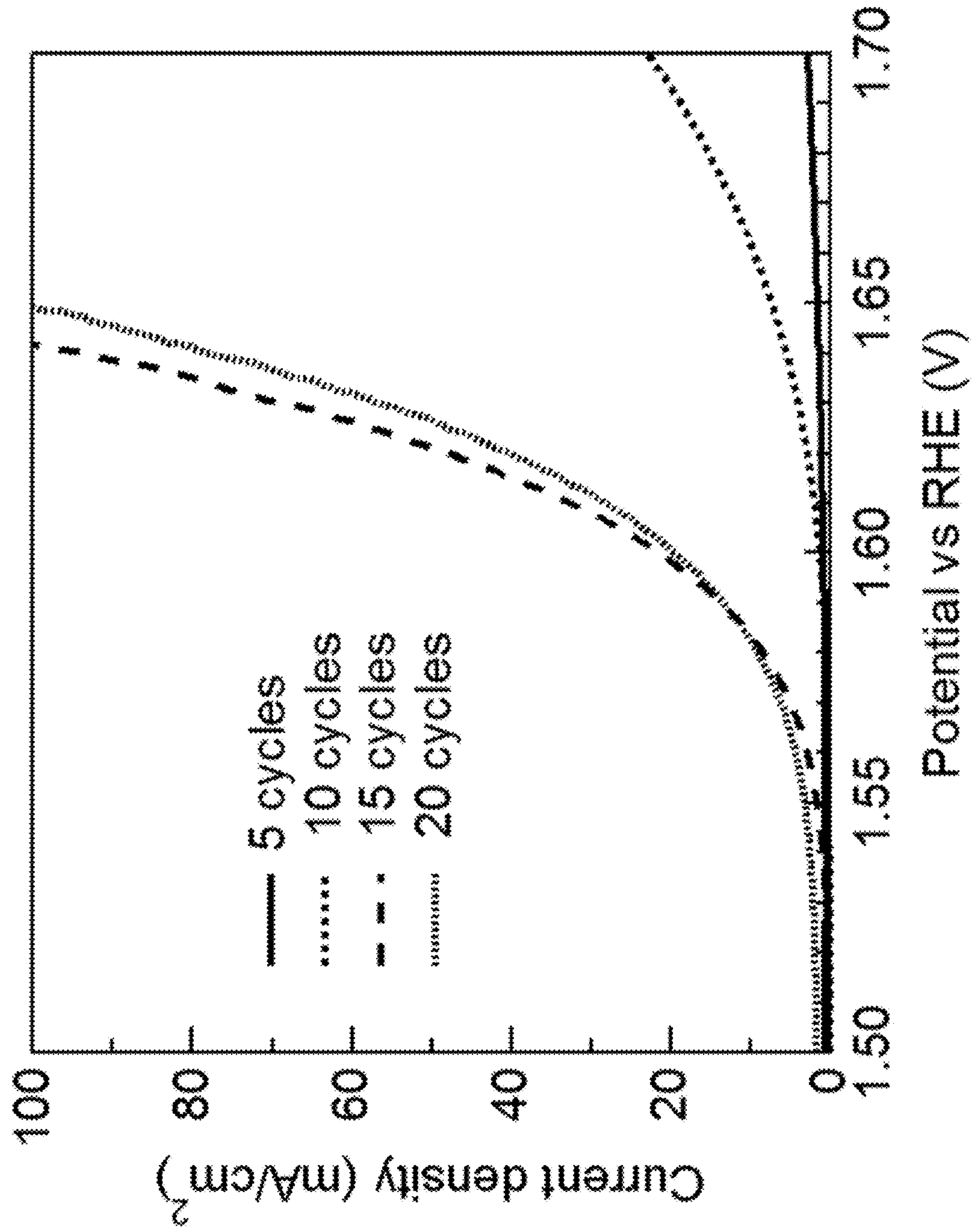


FIG. 12(b)

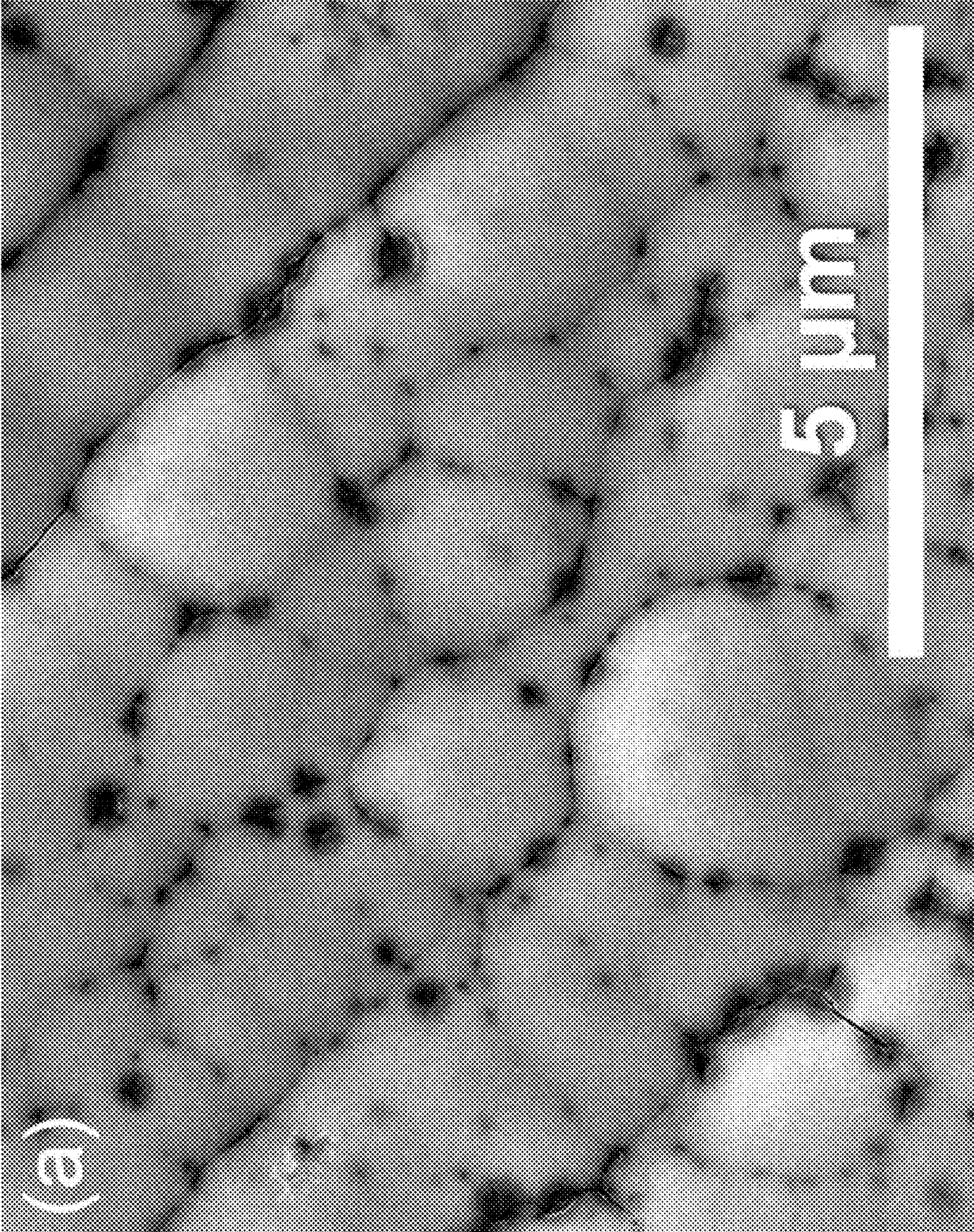


Fig. 13(a)

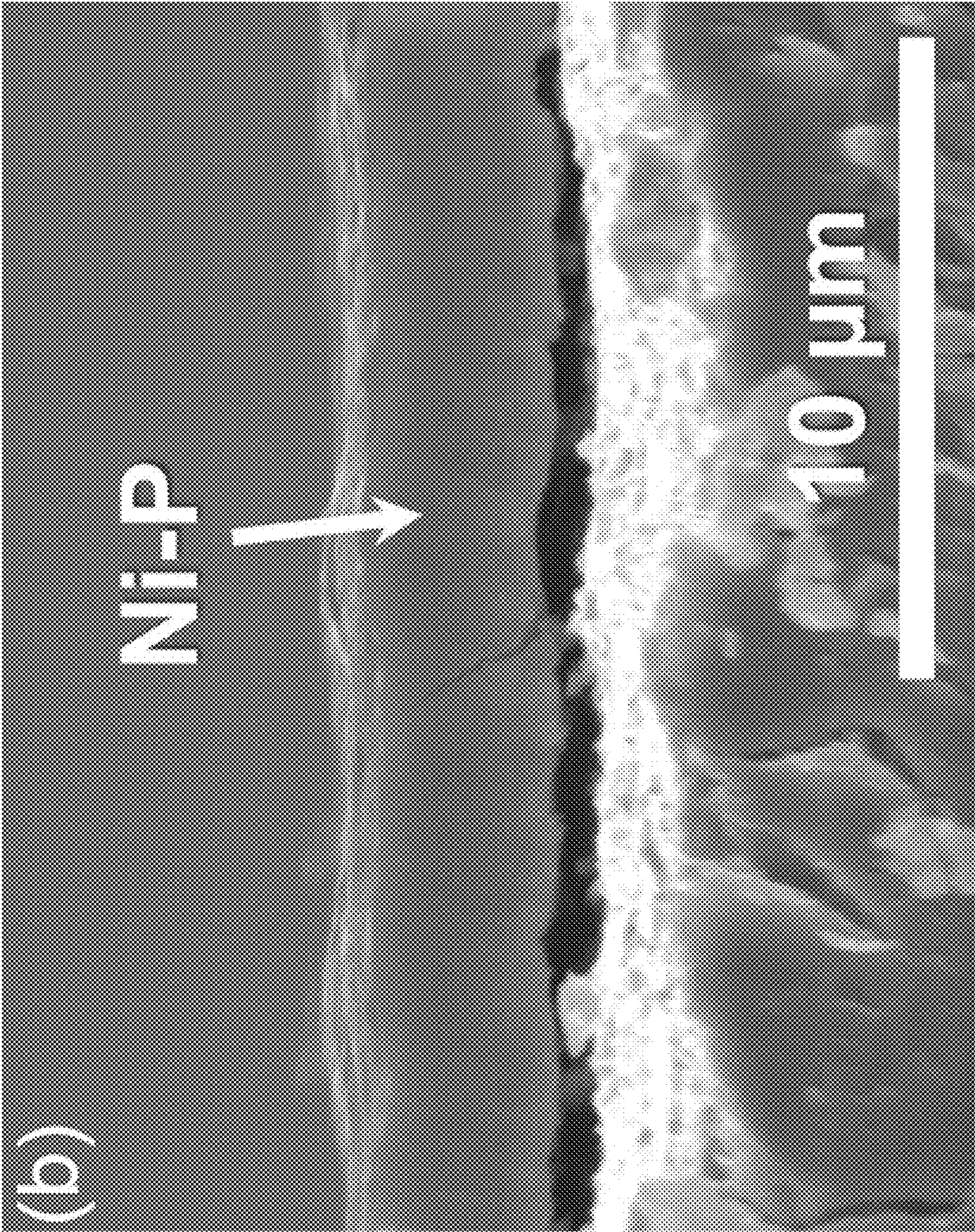


Fig. 13(b)

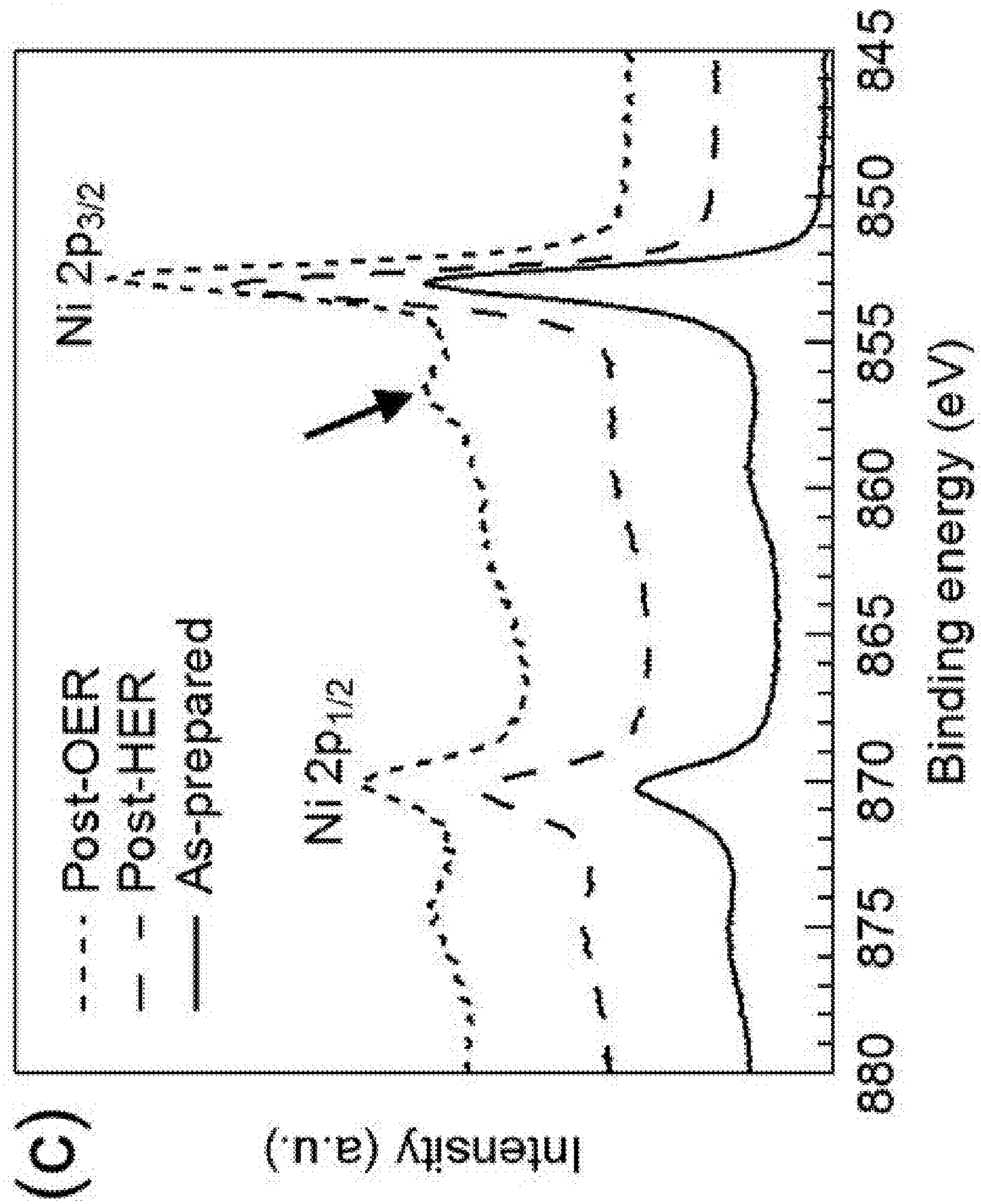


Fig. 13(c)

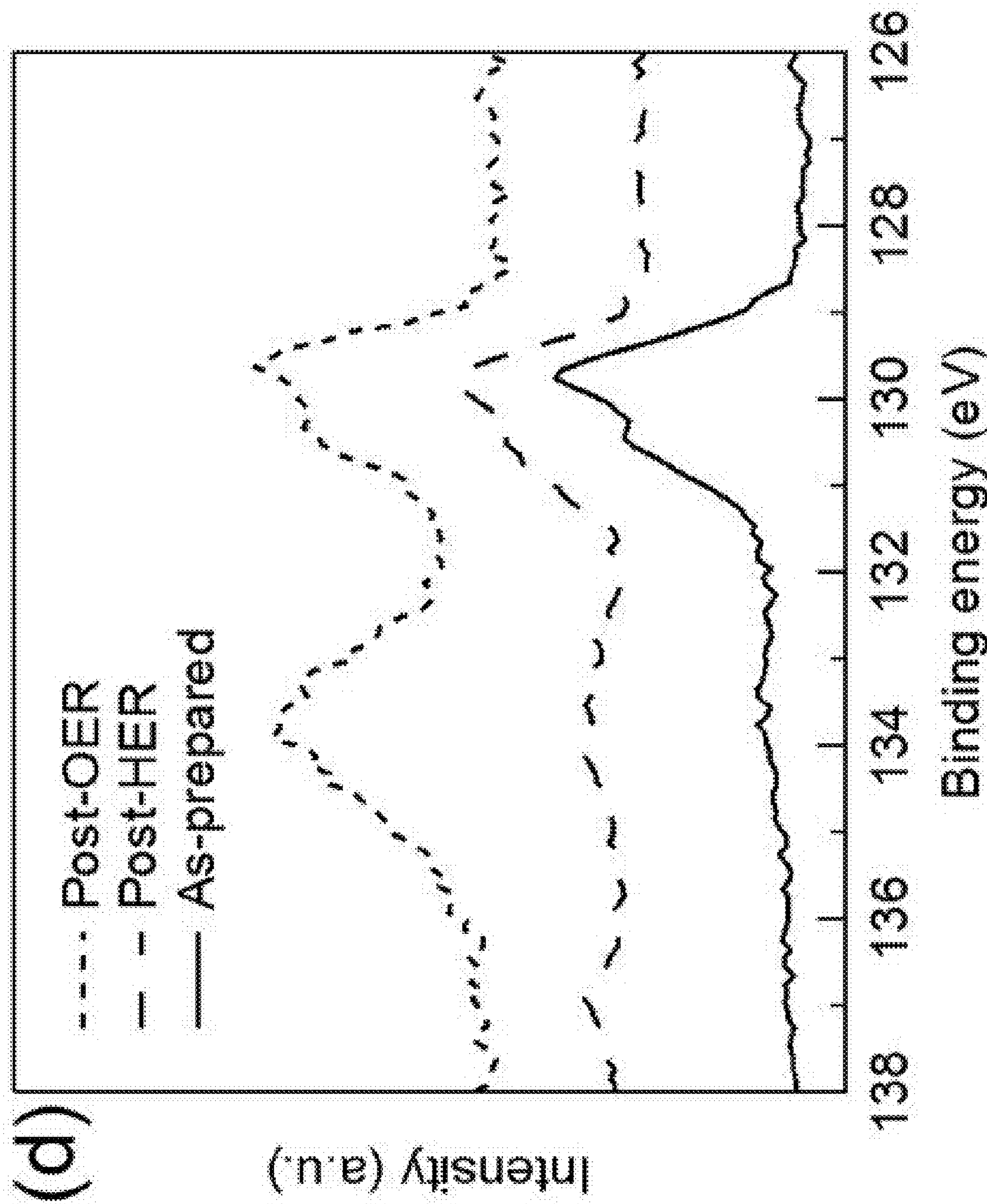


Fig. 13(d)

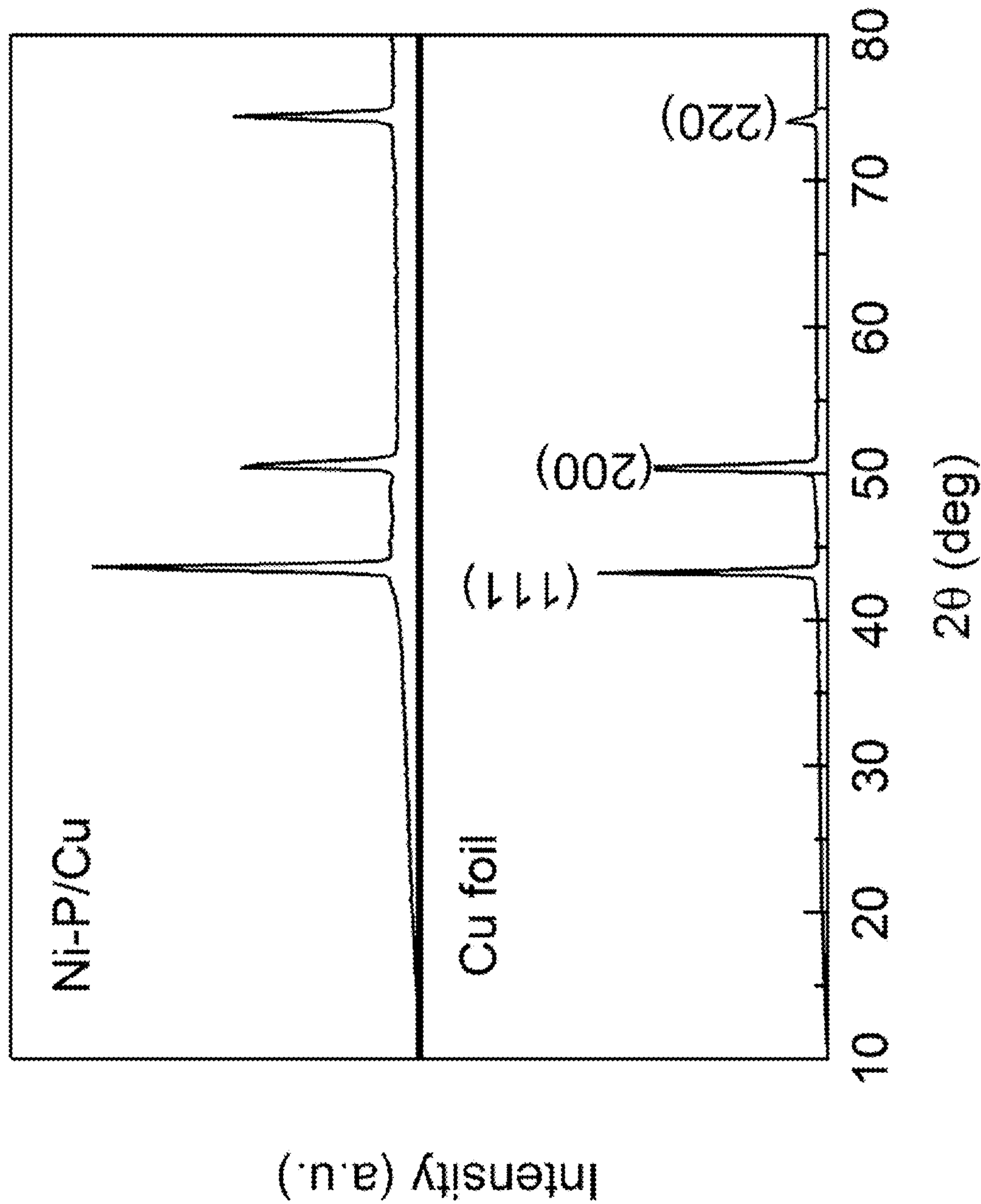


Fig. 14

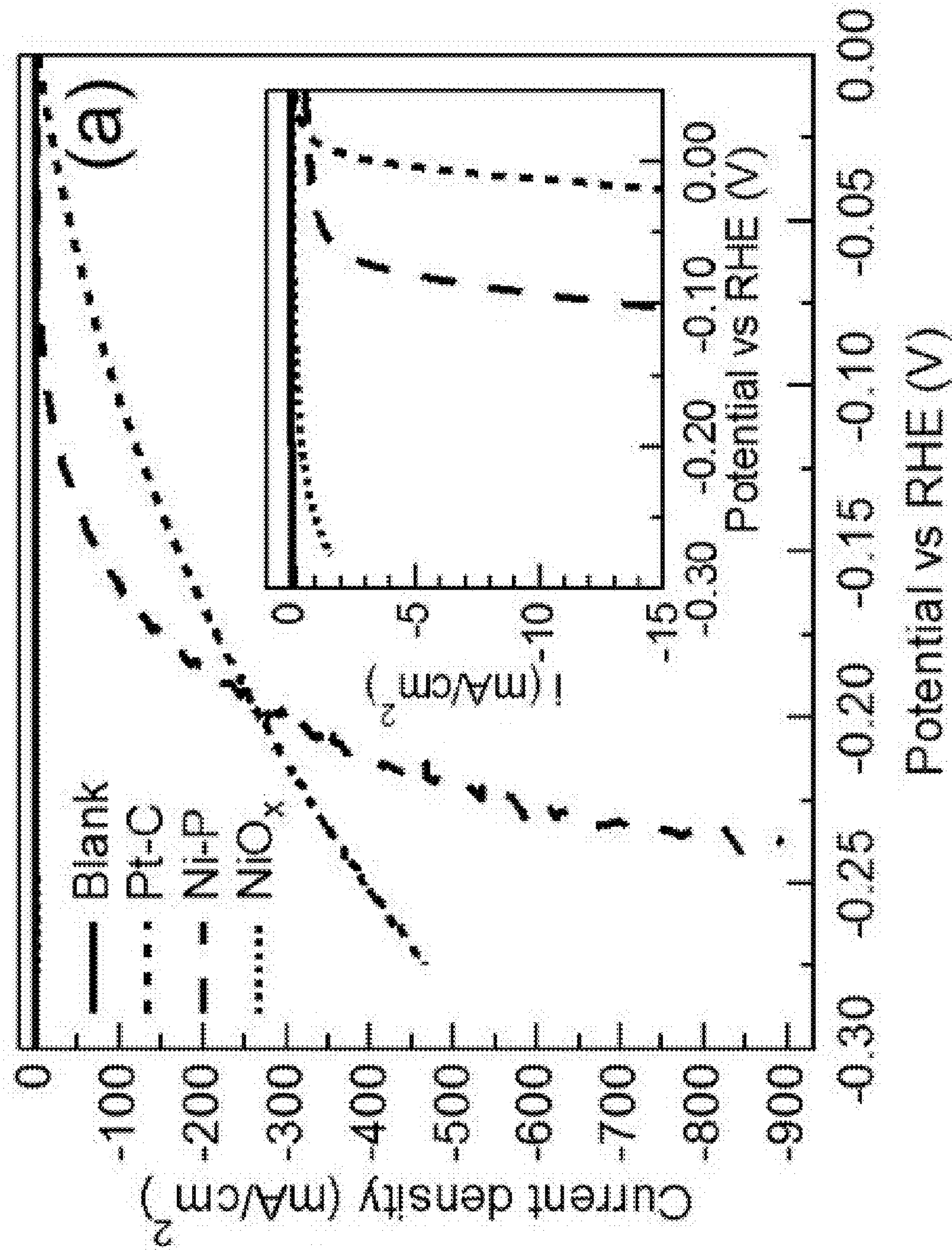


Fig. 15(a)

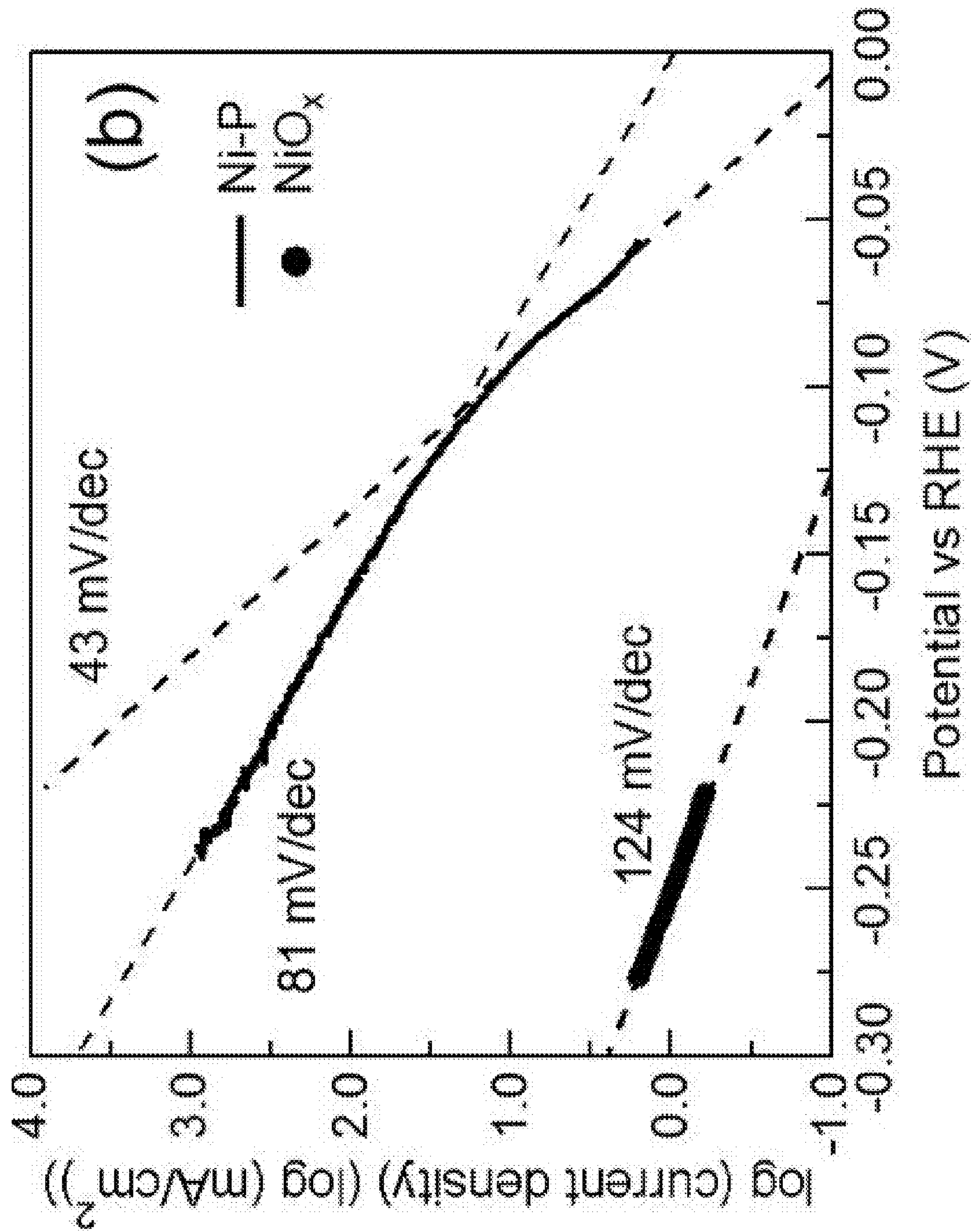


Fig. 15(b)

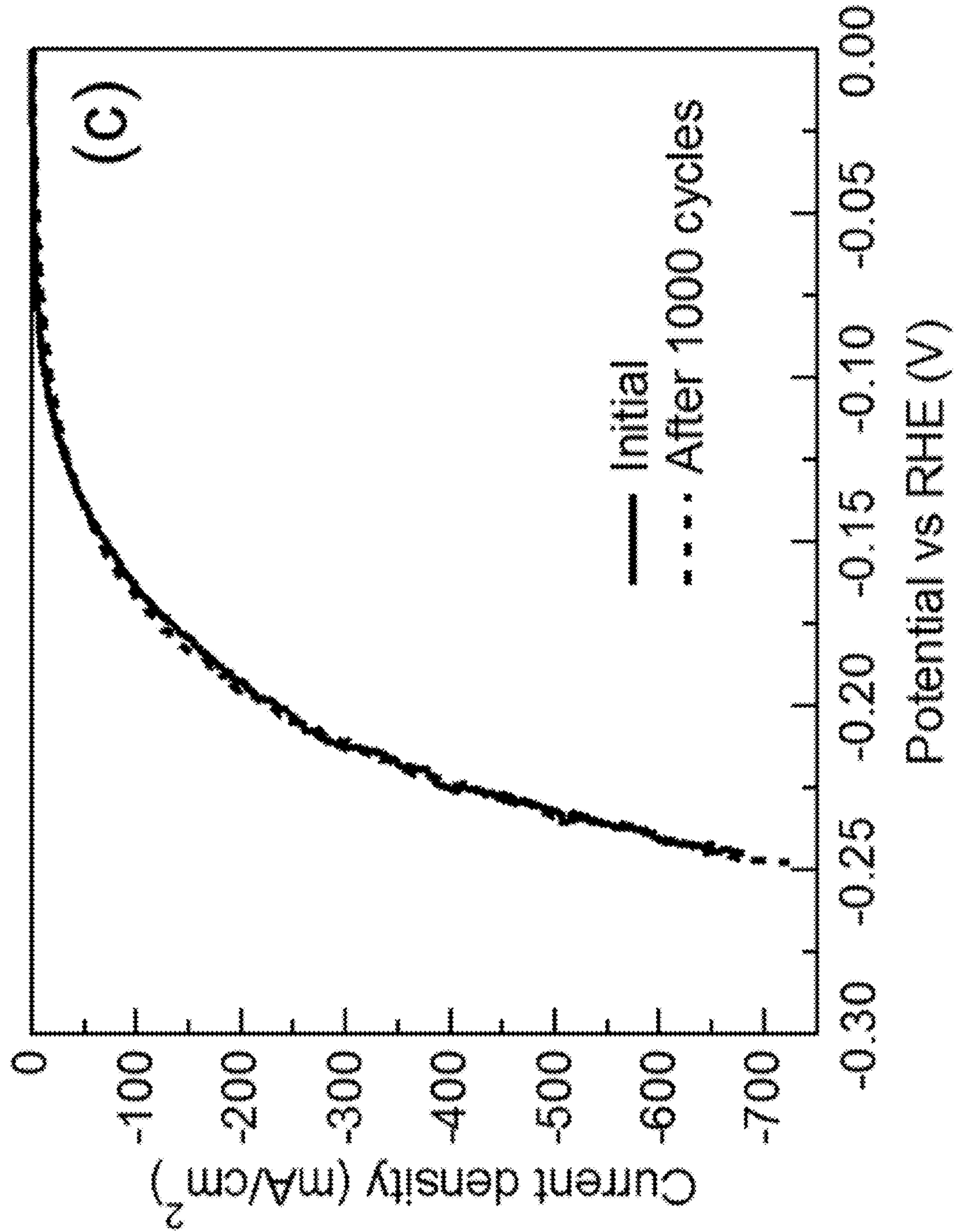


Fig. 15(c)

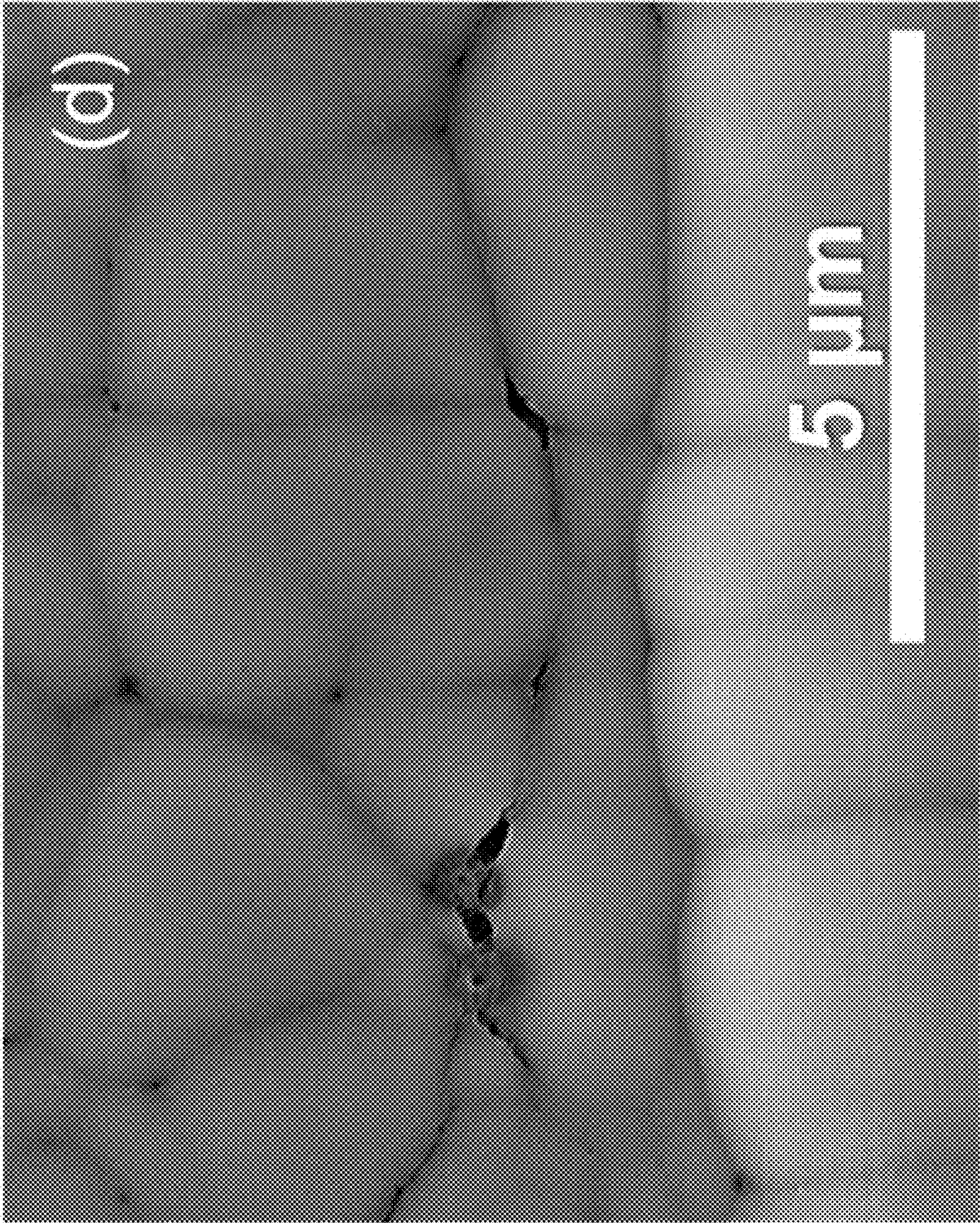


Fig. 15(d)

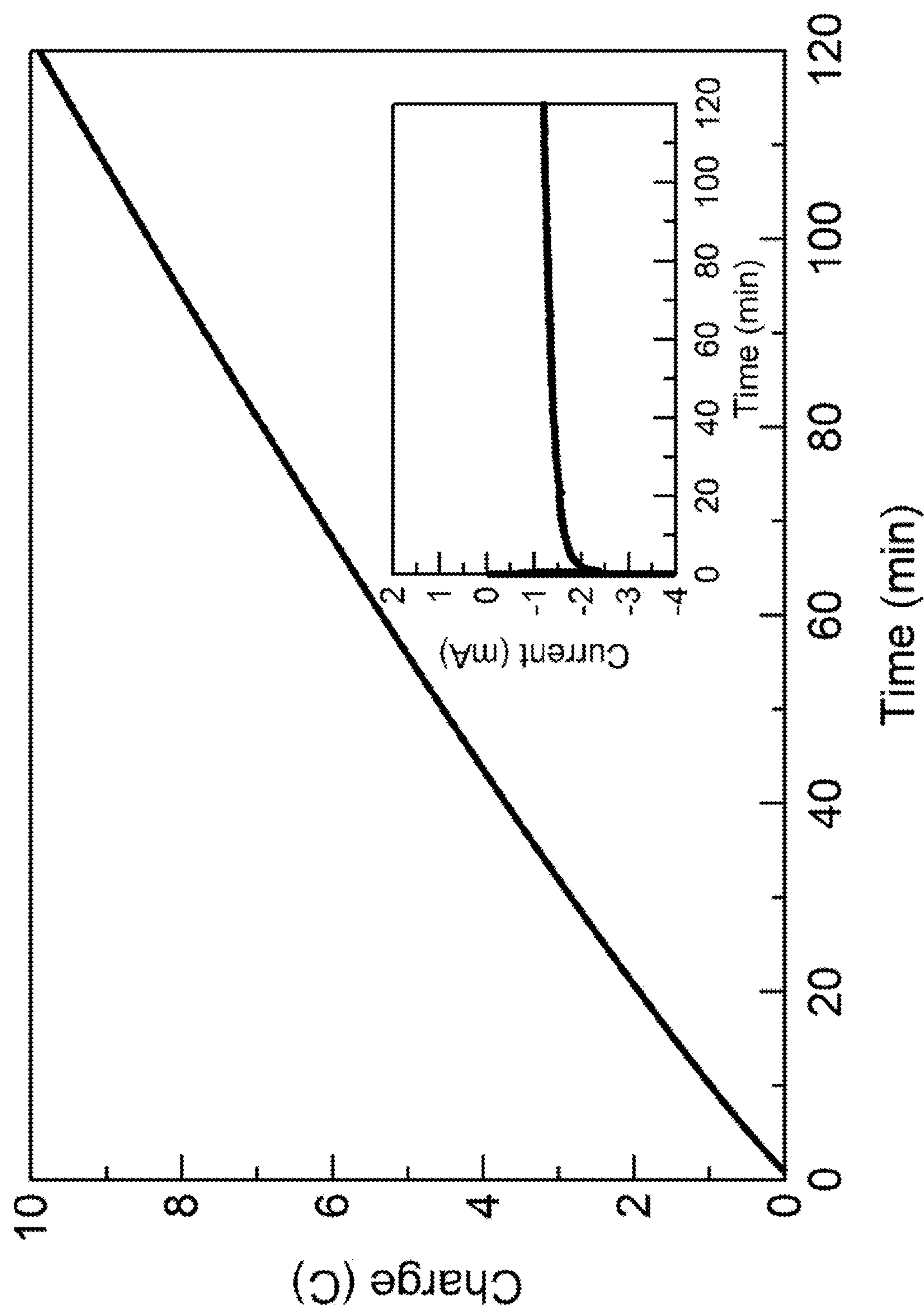


Fig. 16

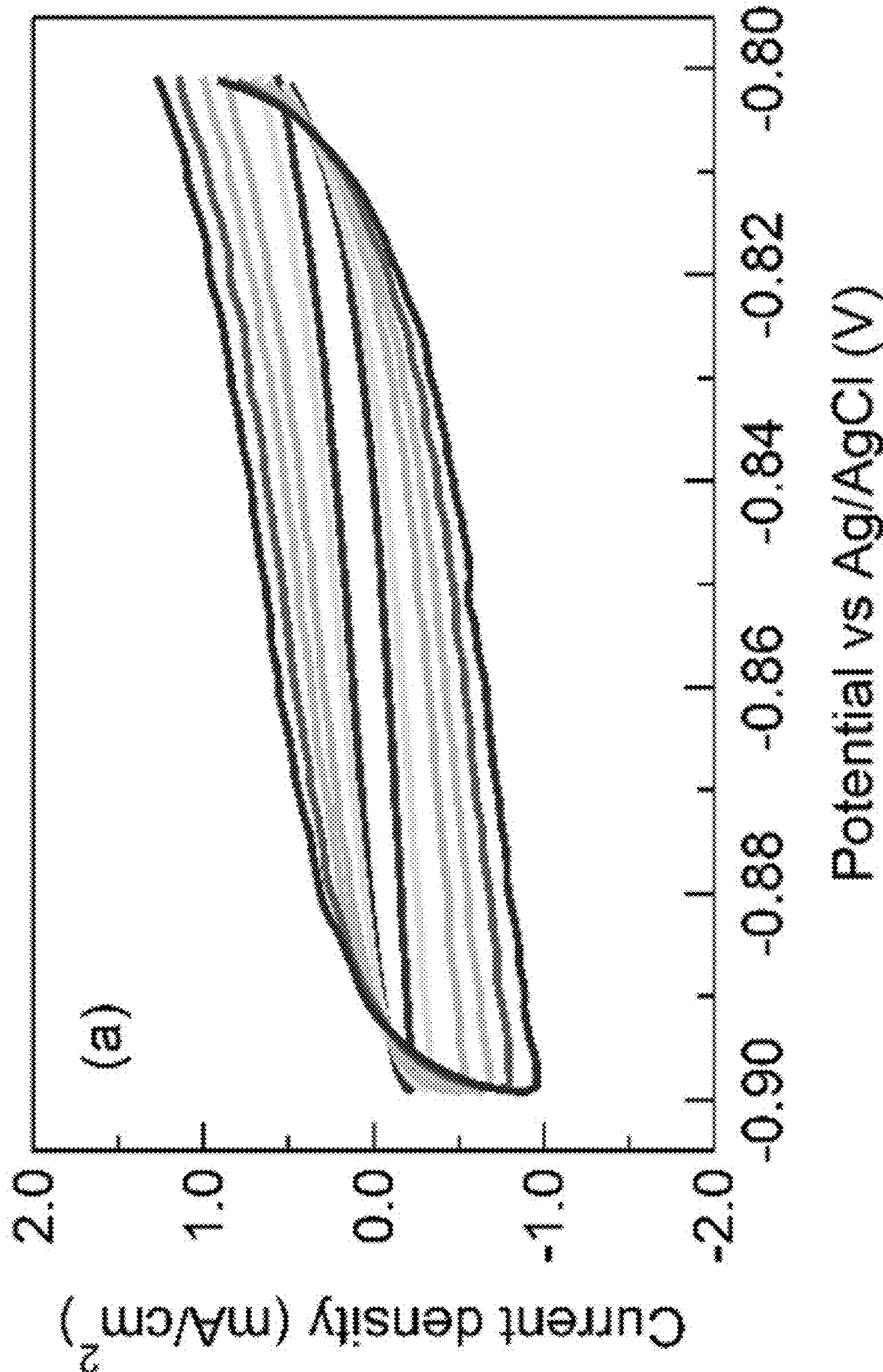


Fig. 17(a)

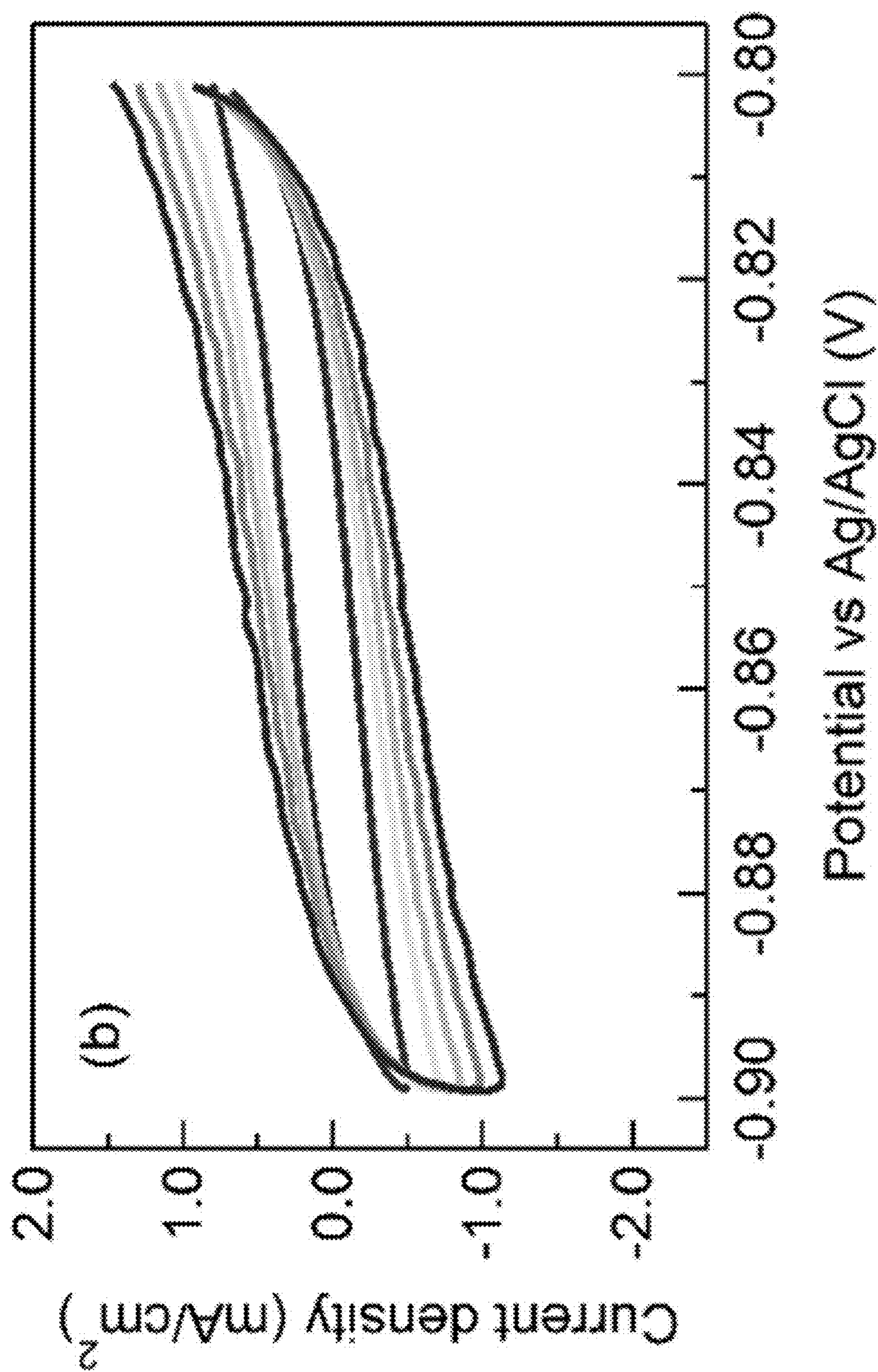


Fig. 17(b)

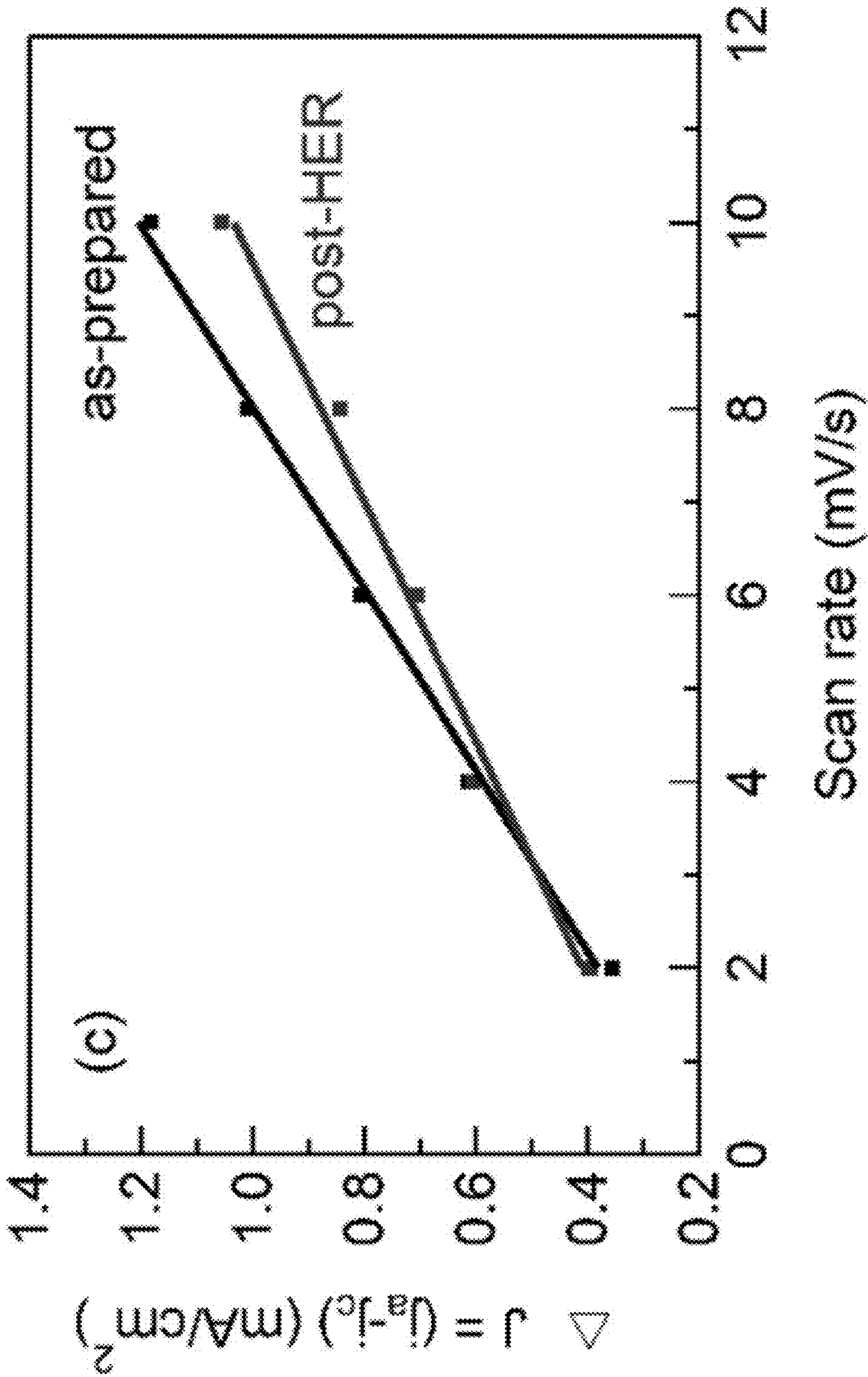


Fig. 17(c)

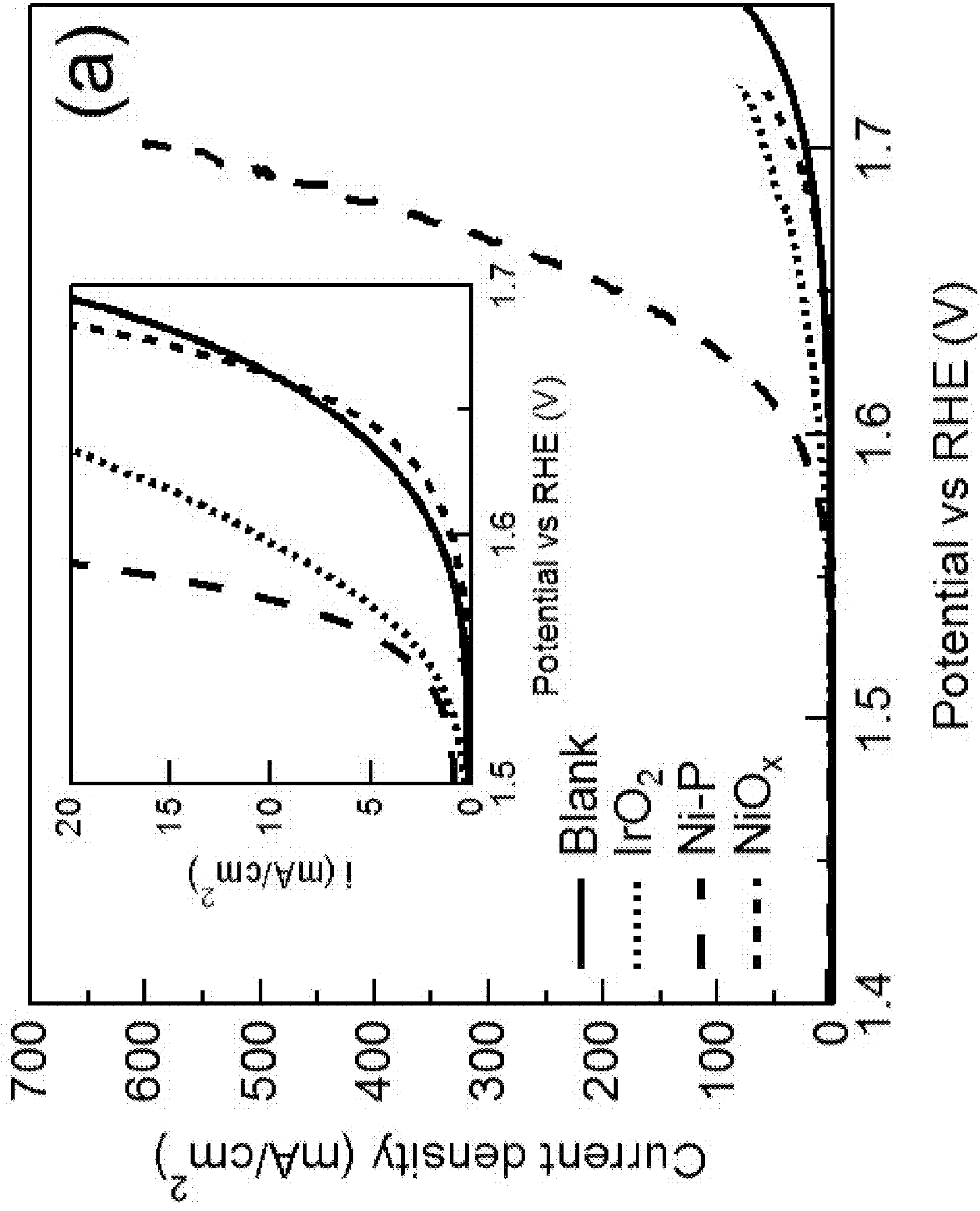


Fig. 18(a)

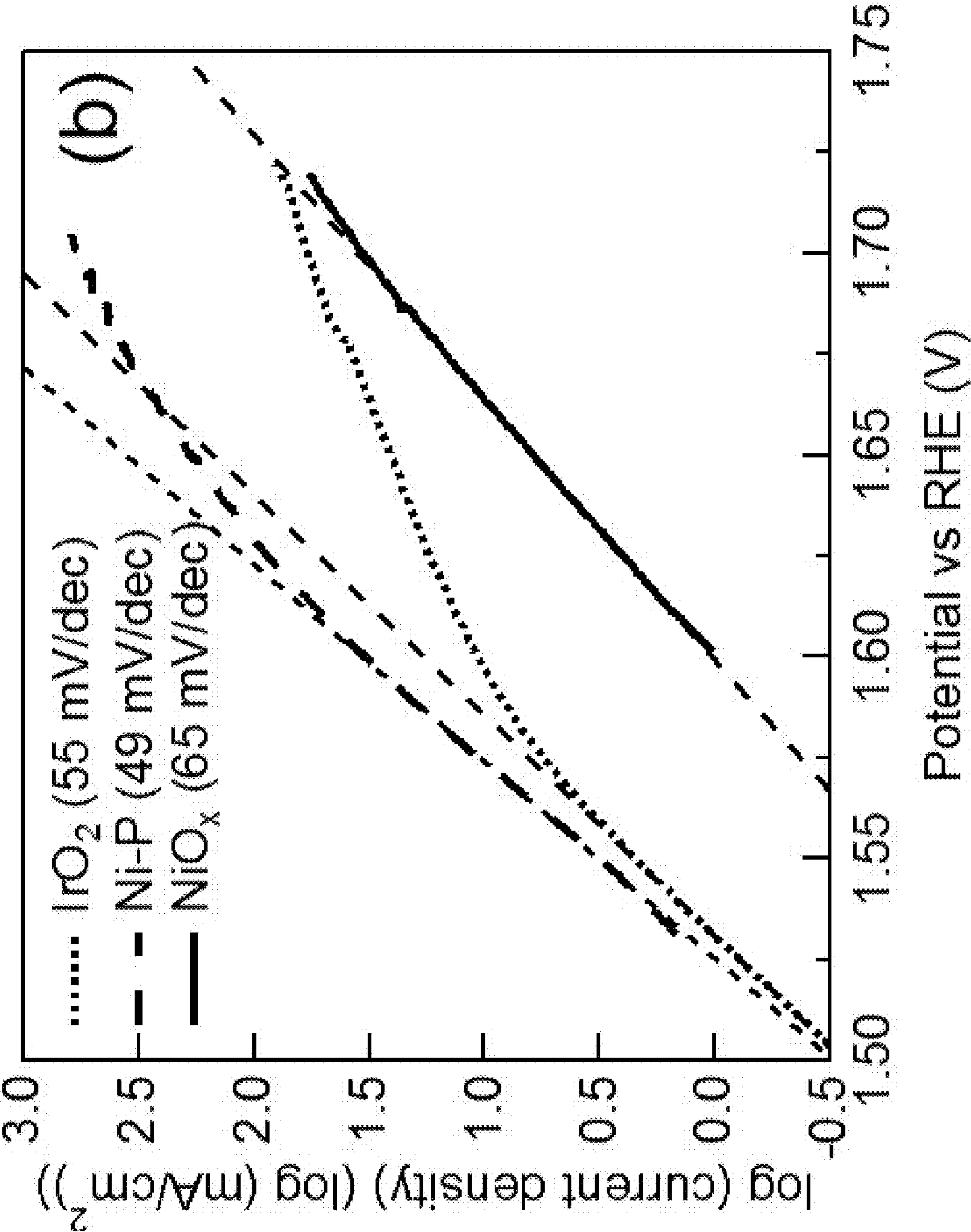


Fig. 18(b)

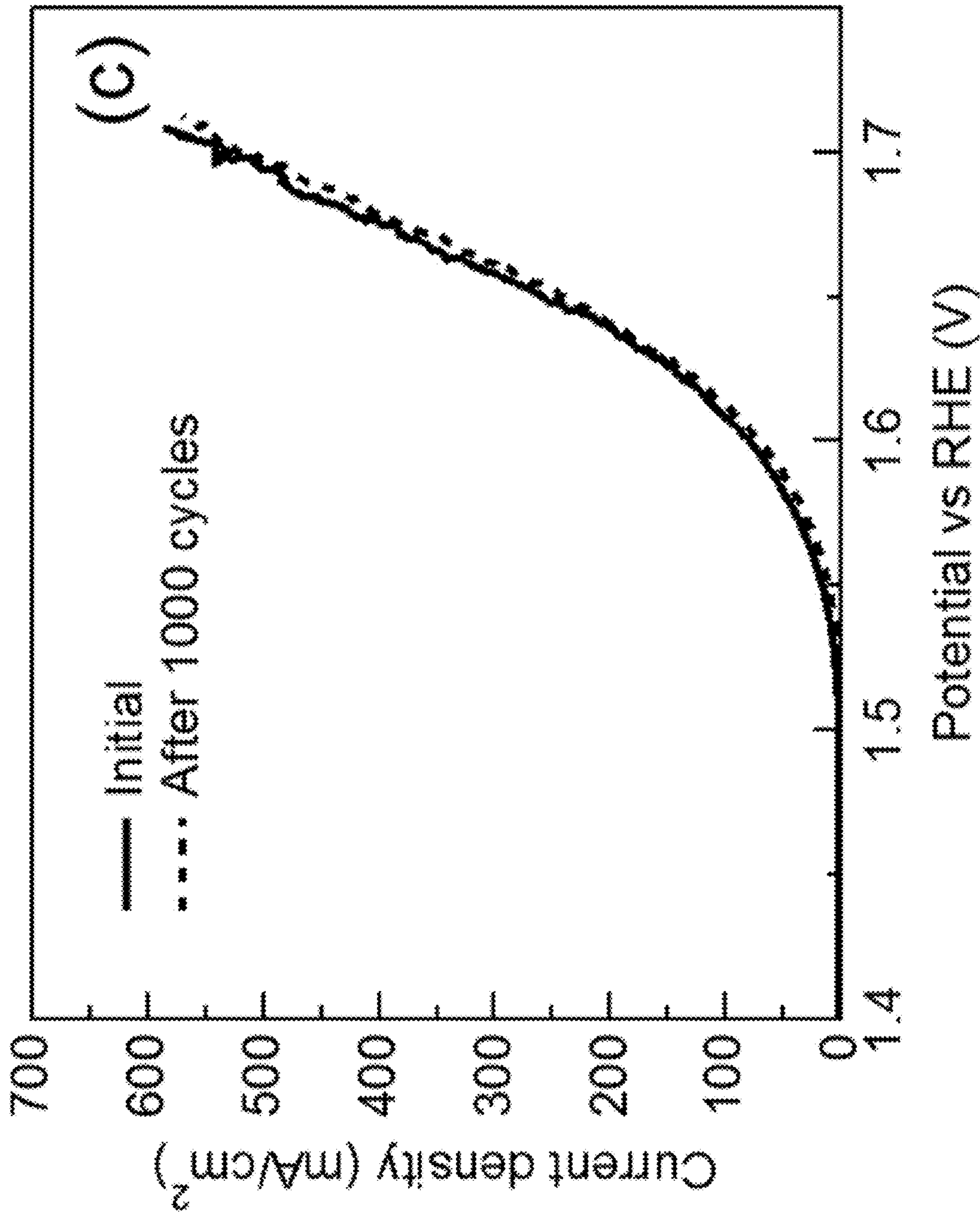


Fig. 18(c)

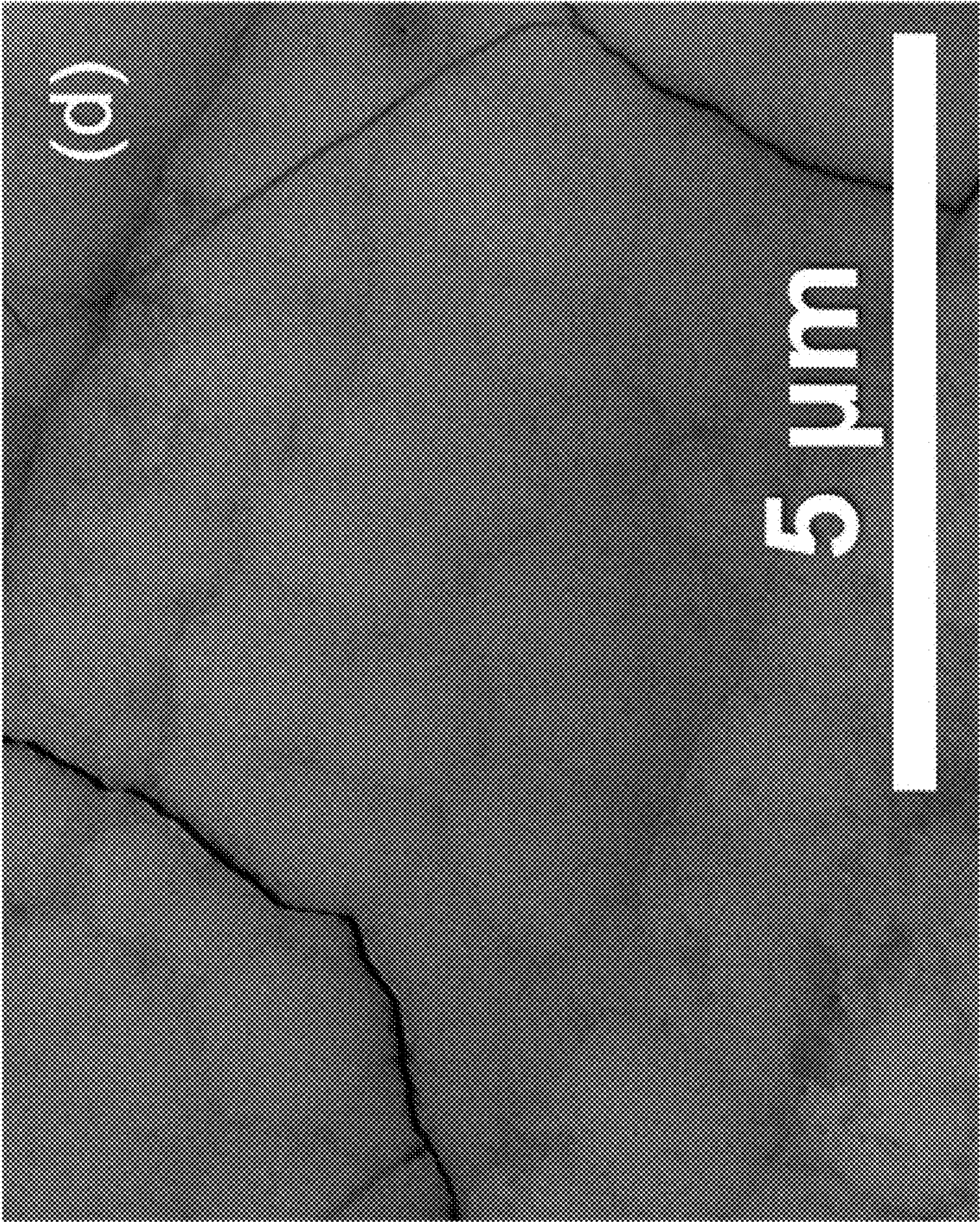


Fig. 18(d)

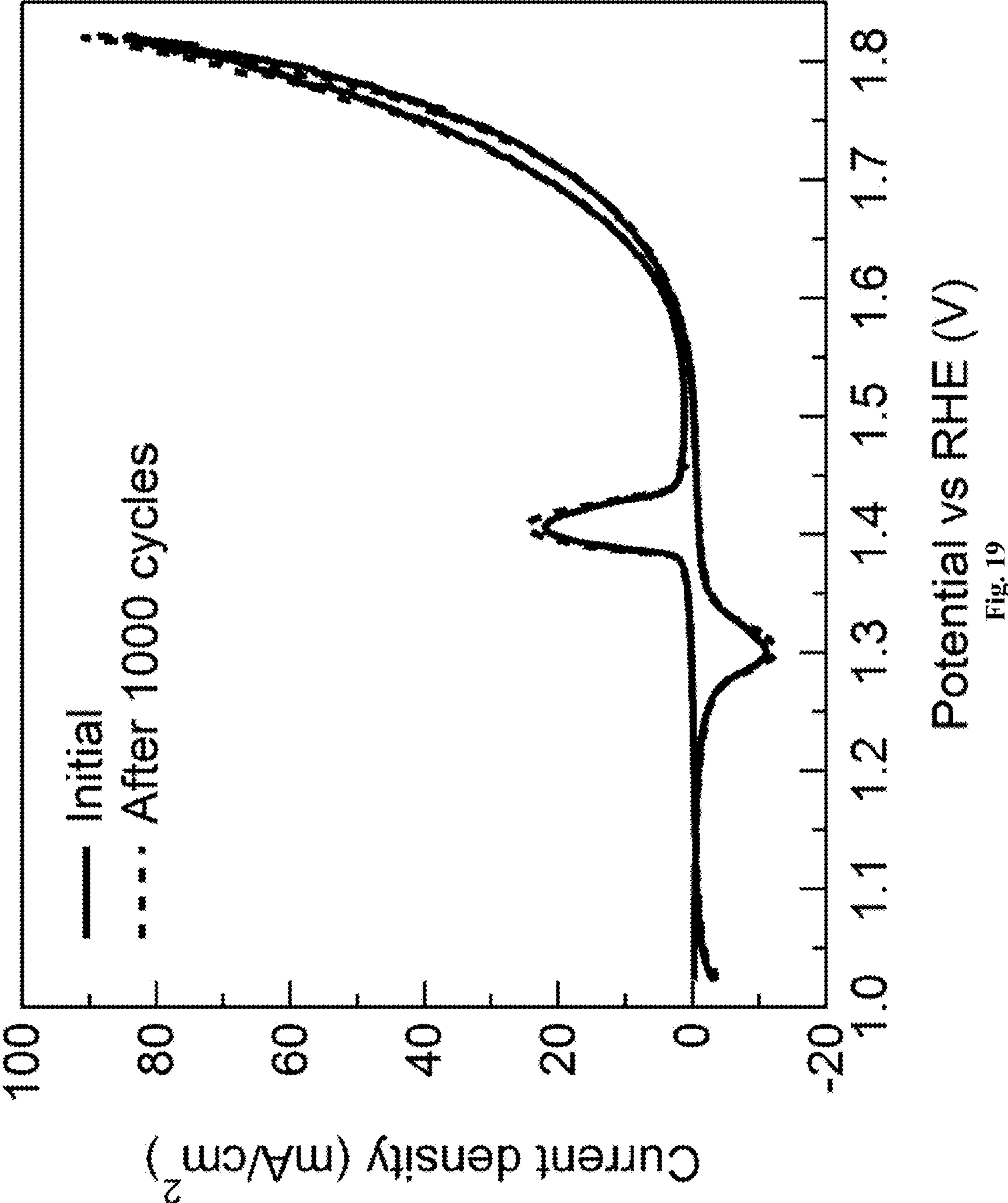


Fig. 19

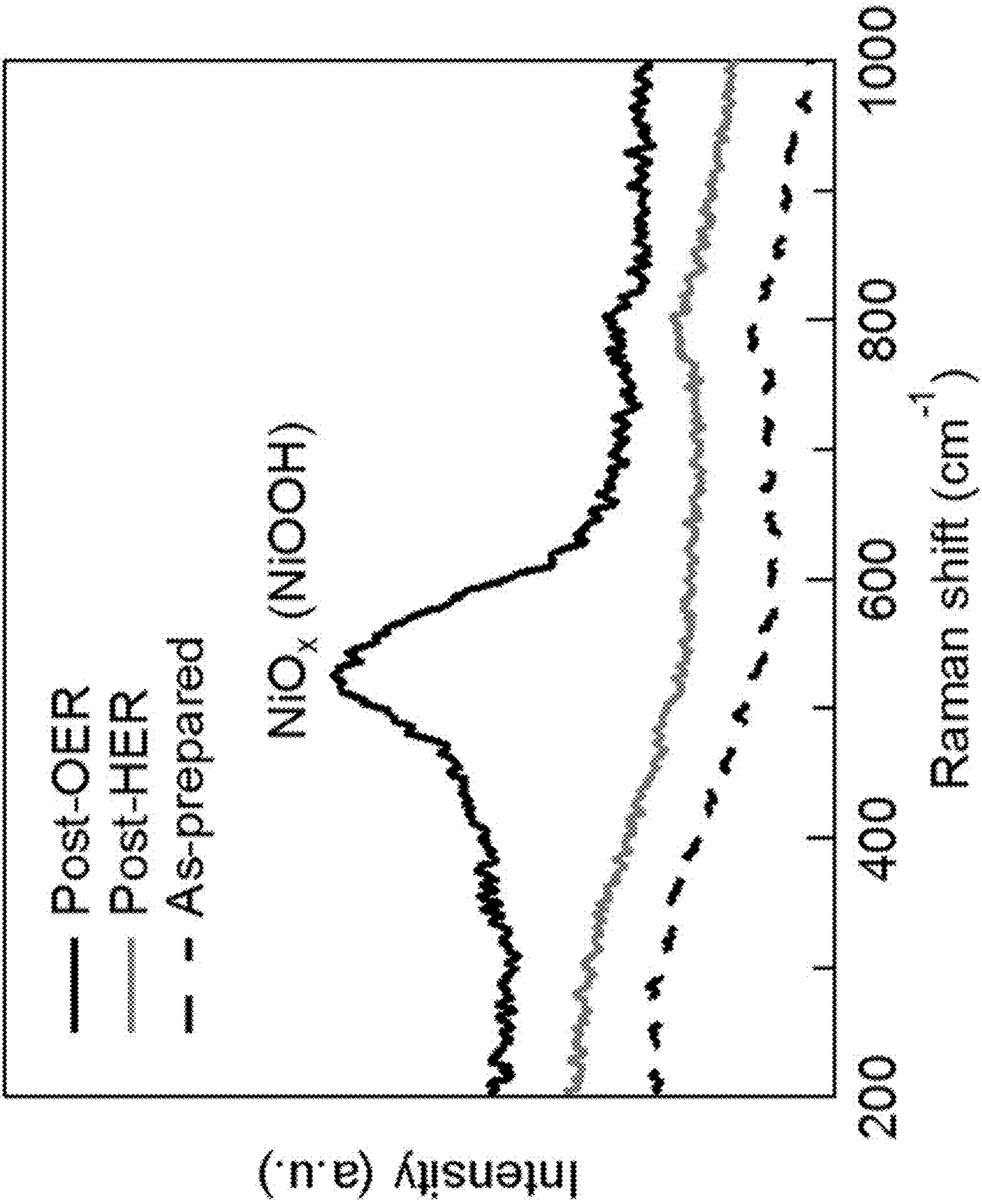


Fig. 20

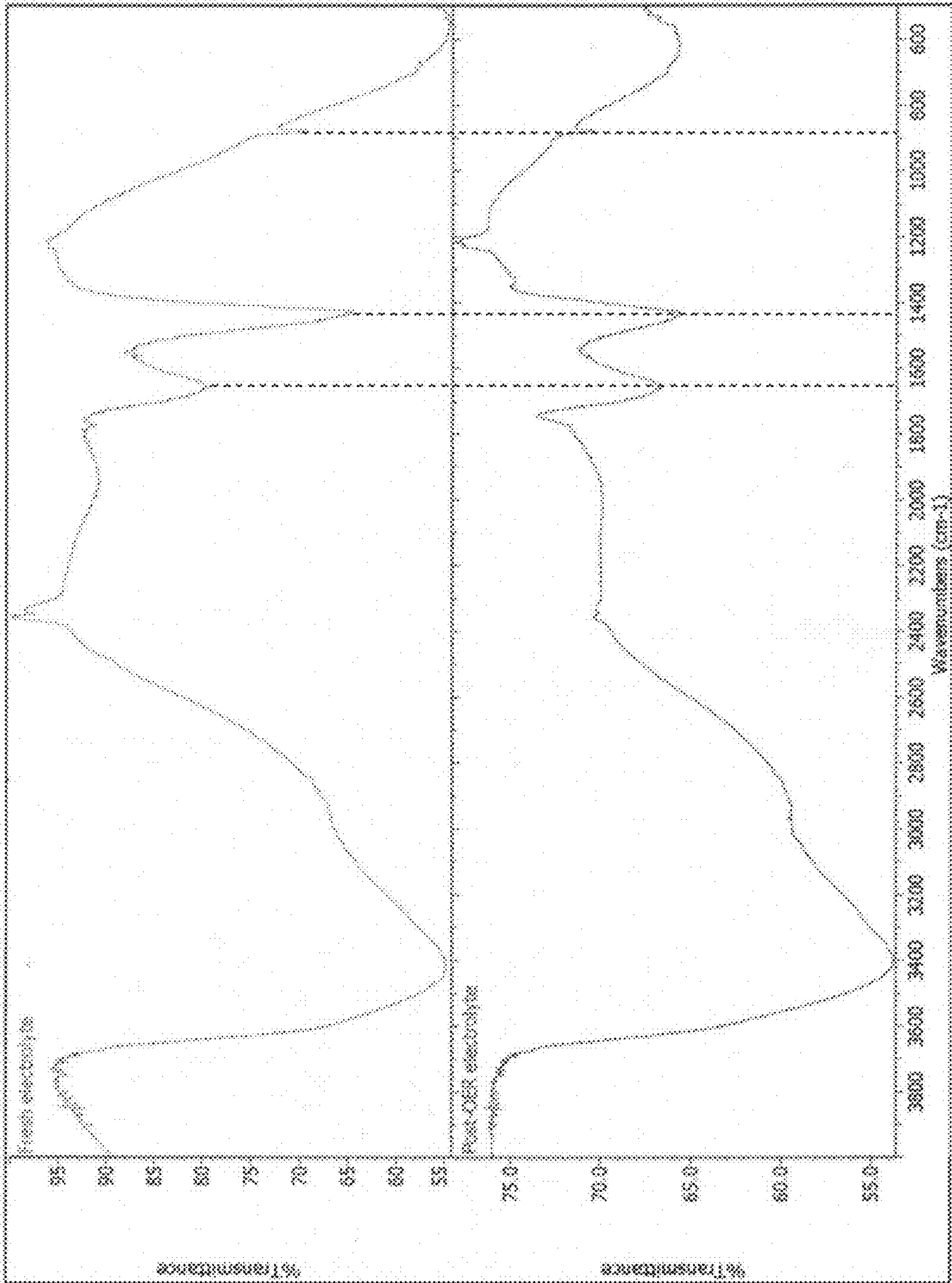


Fig. 21

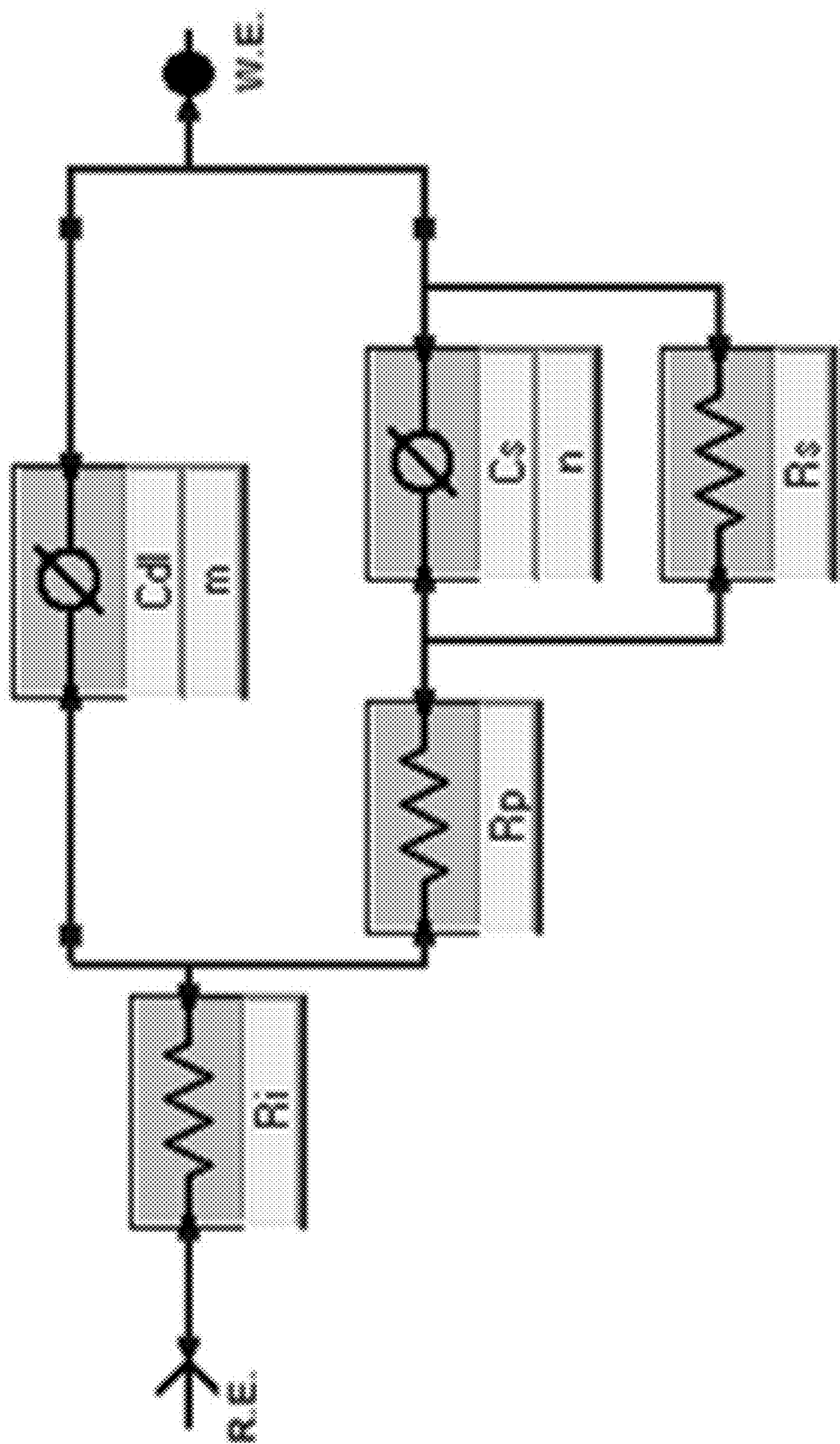


FIG. 22

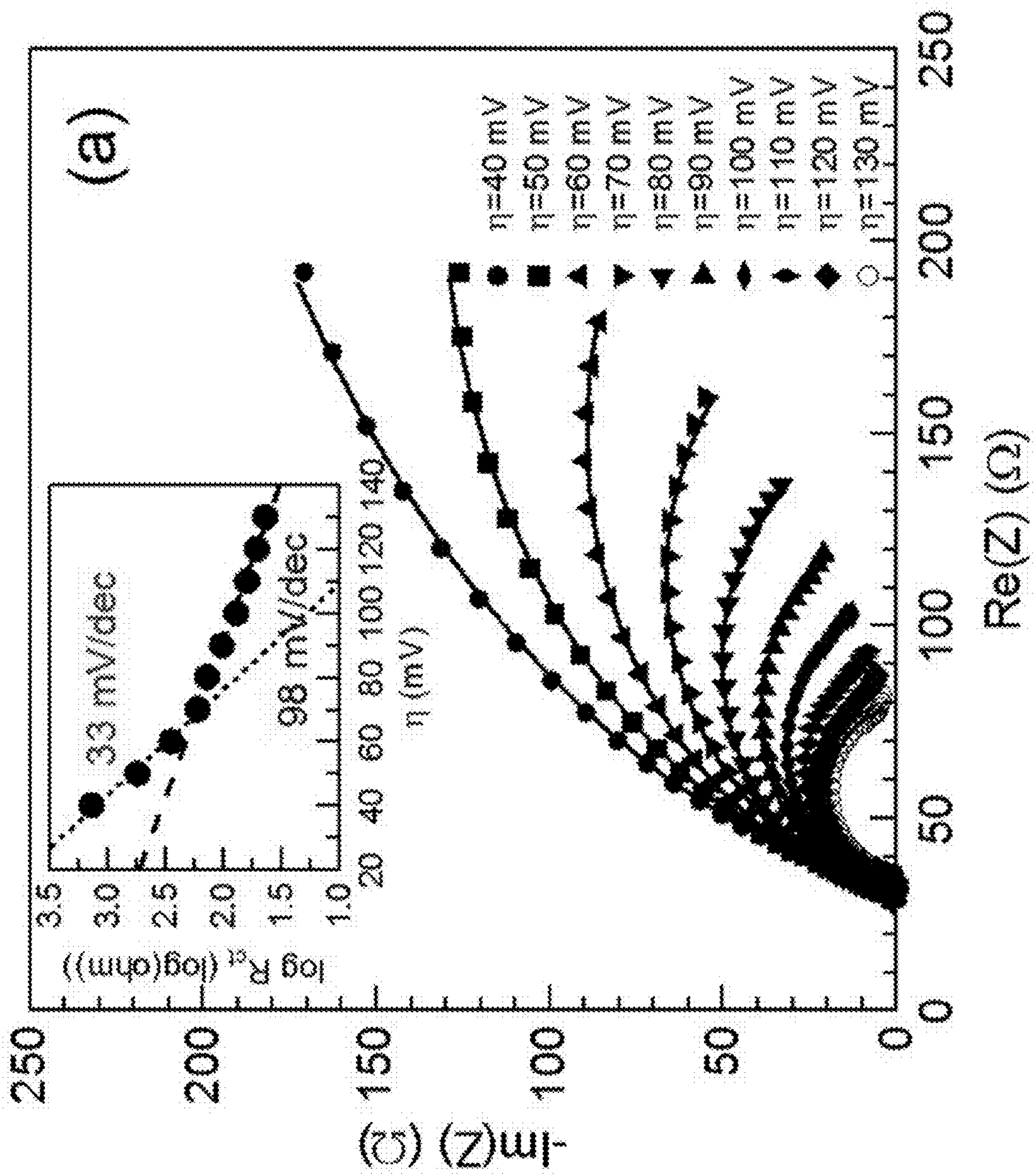


FIG. 23(a)

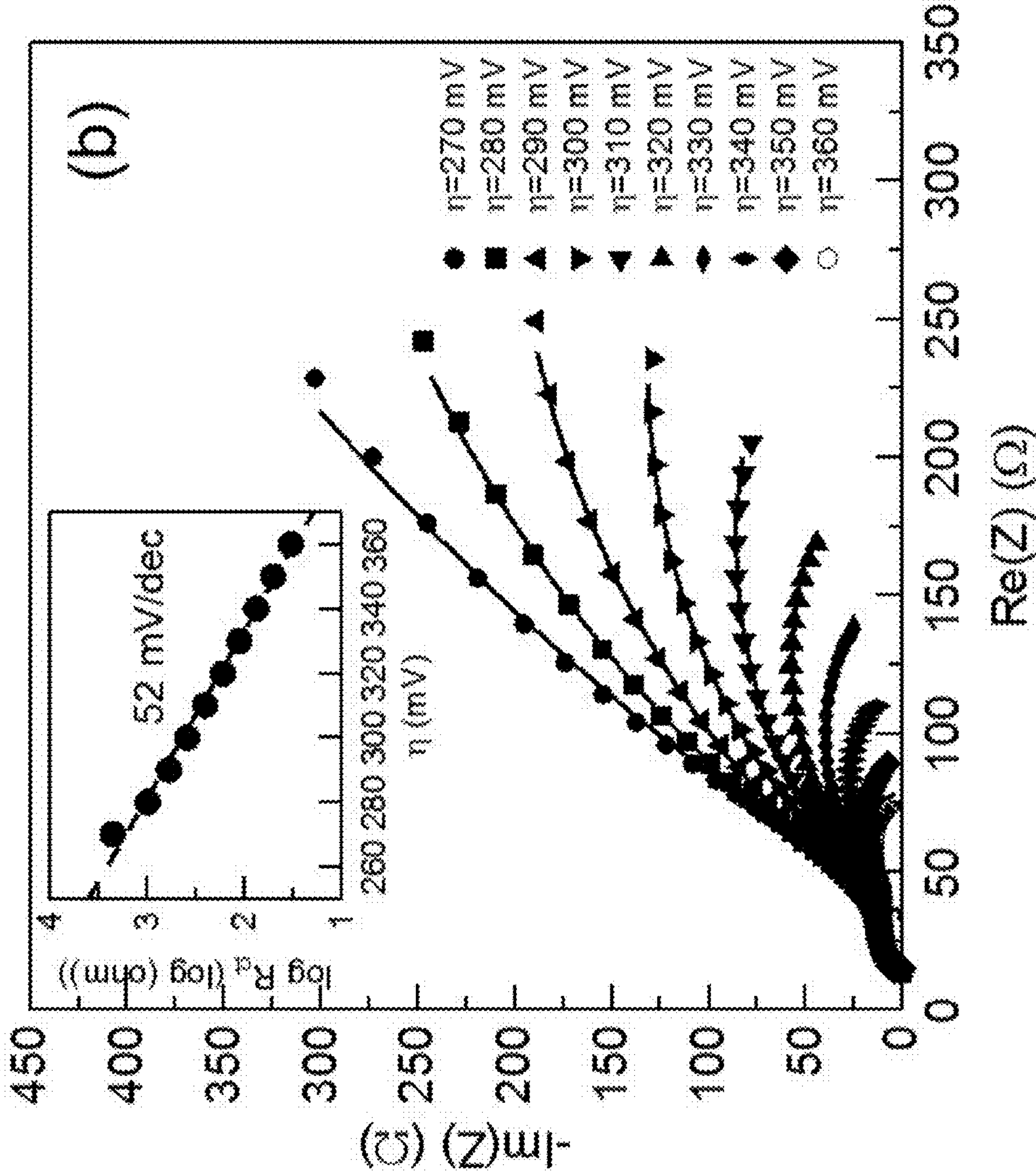


FIG. 23(b)

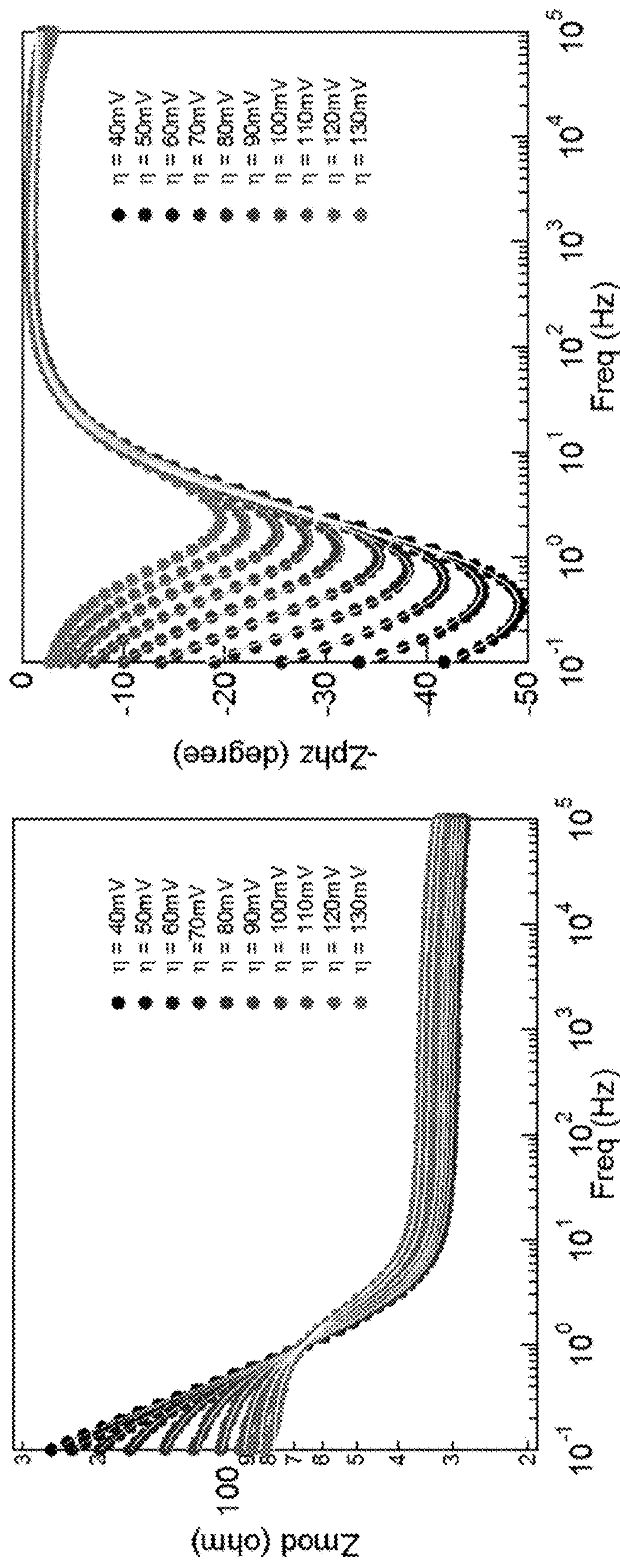


FIG. 24

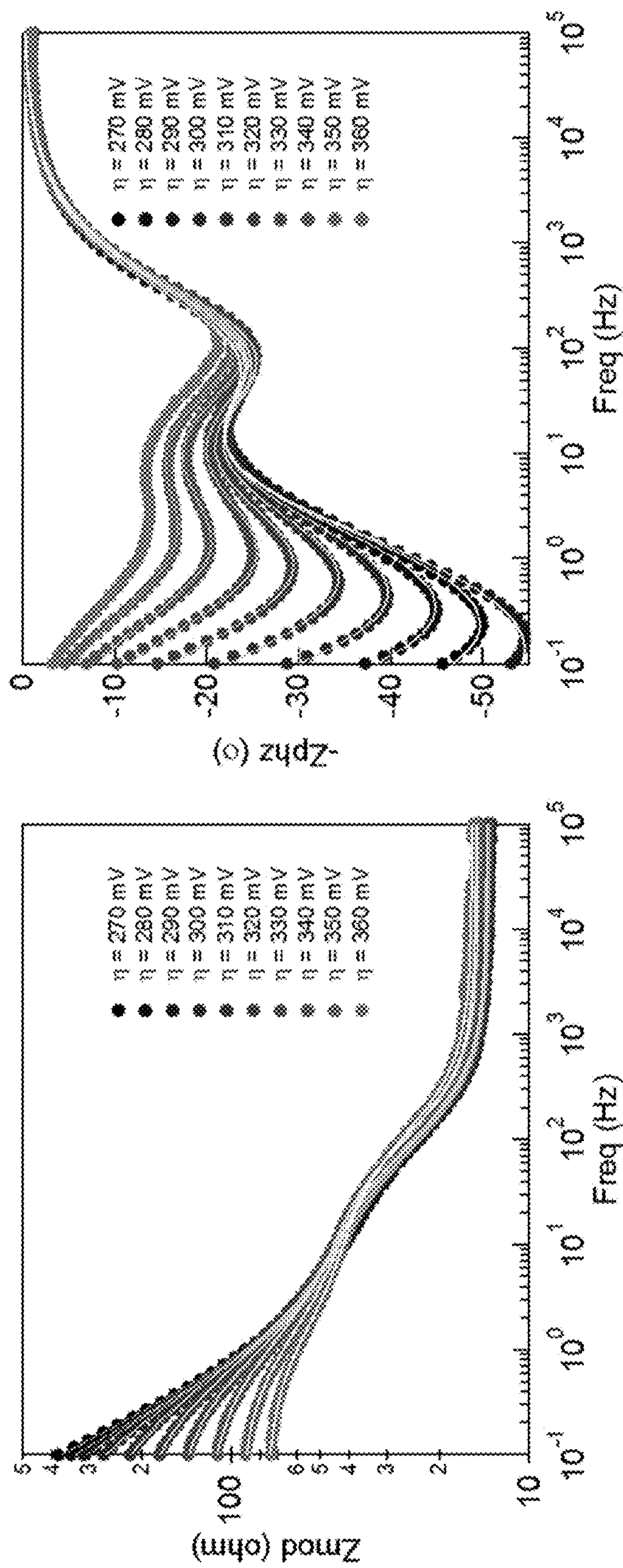


FIG. 25

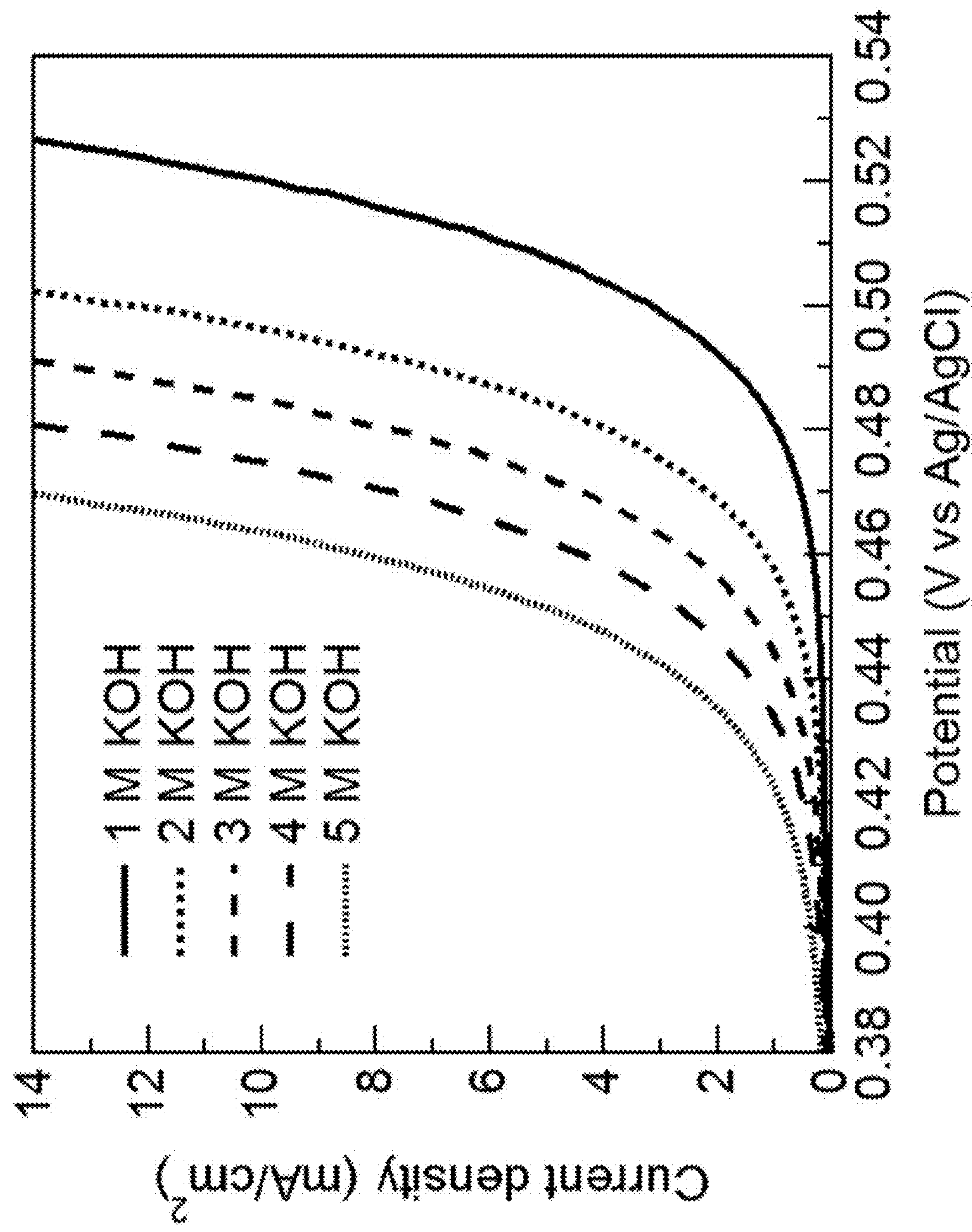


FIG. 26

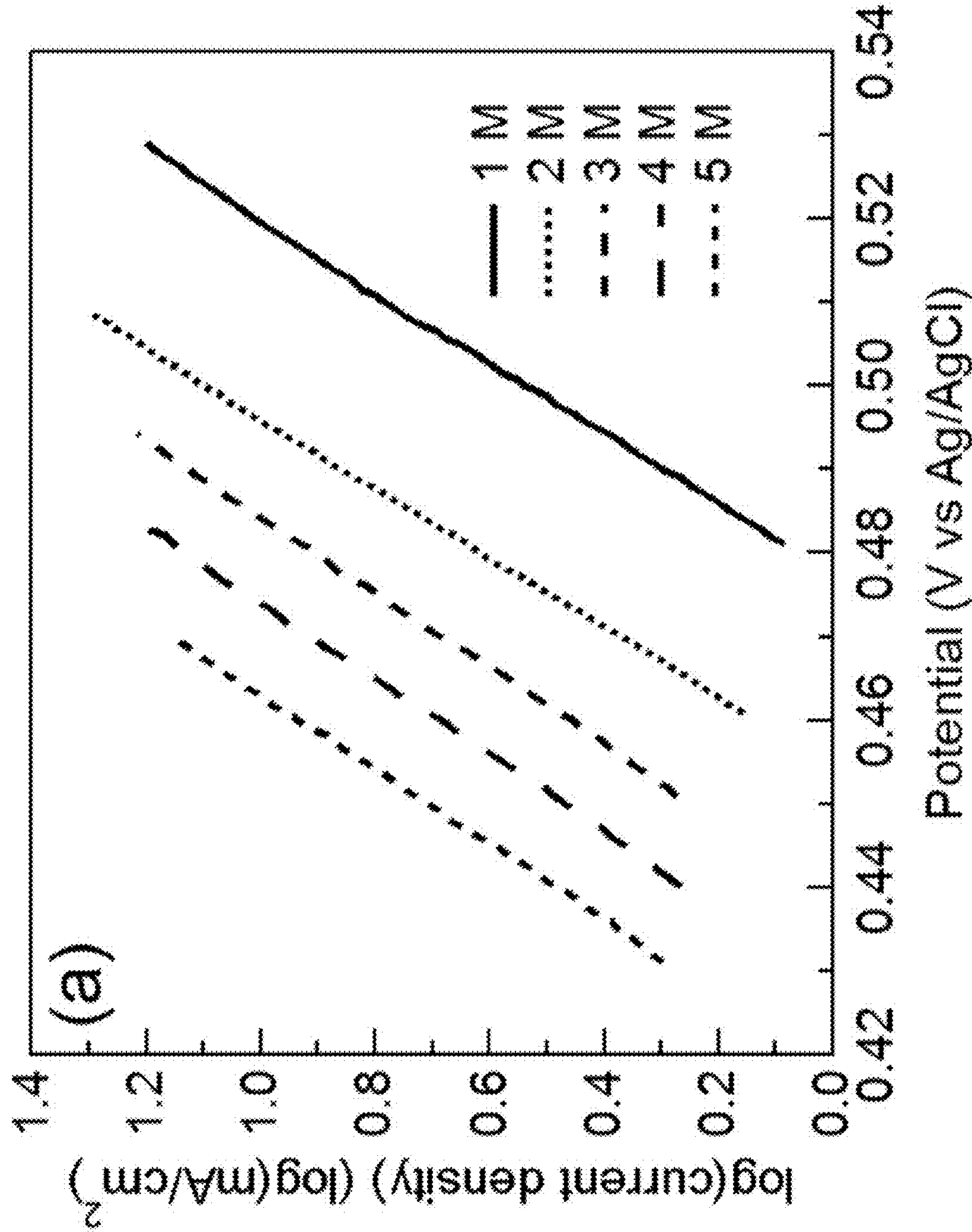


FIG. 27(a)

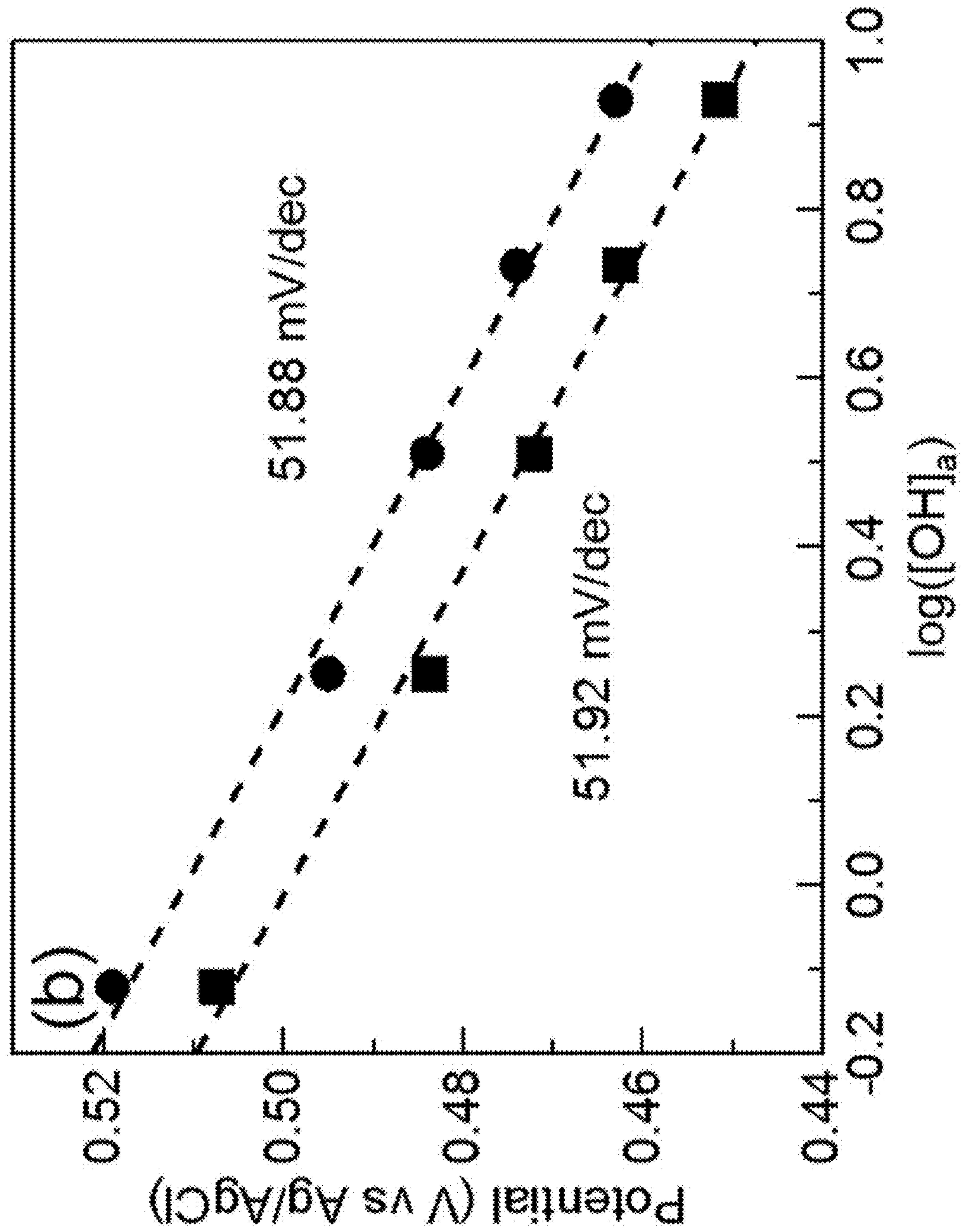


FIG. 27(b)

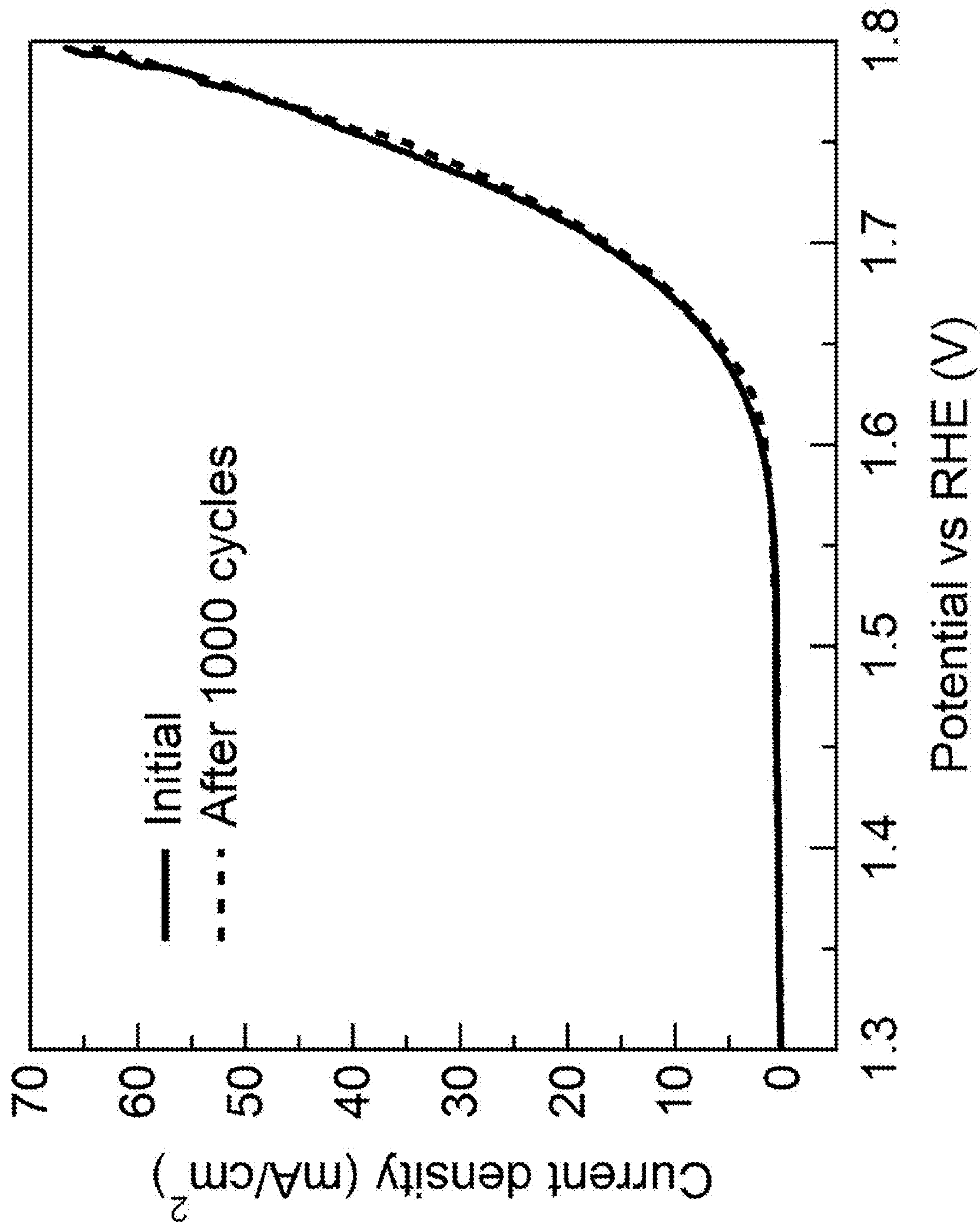
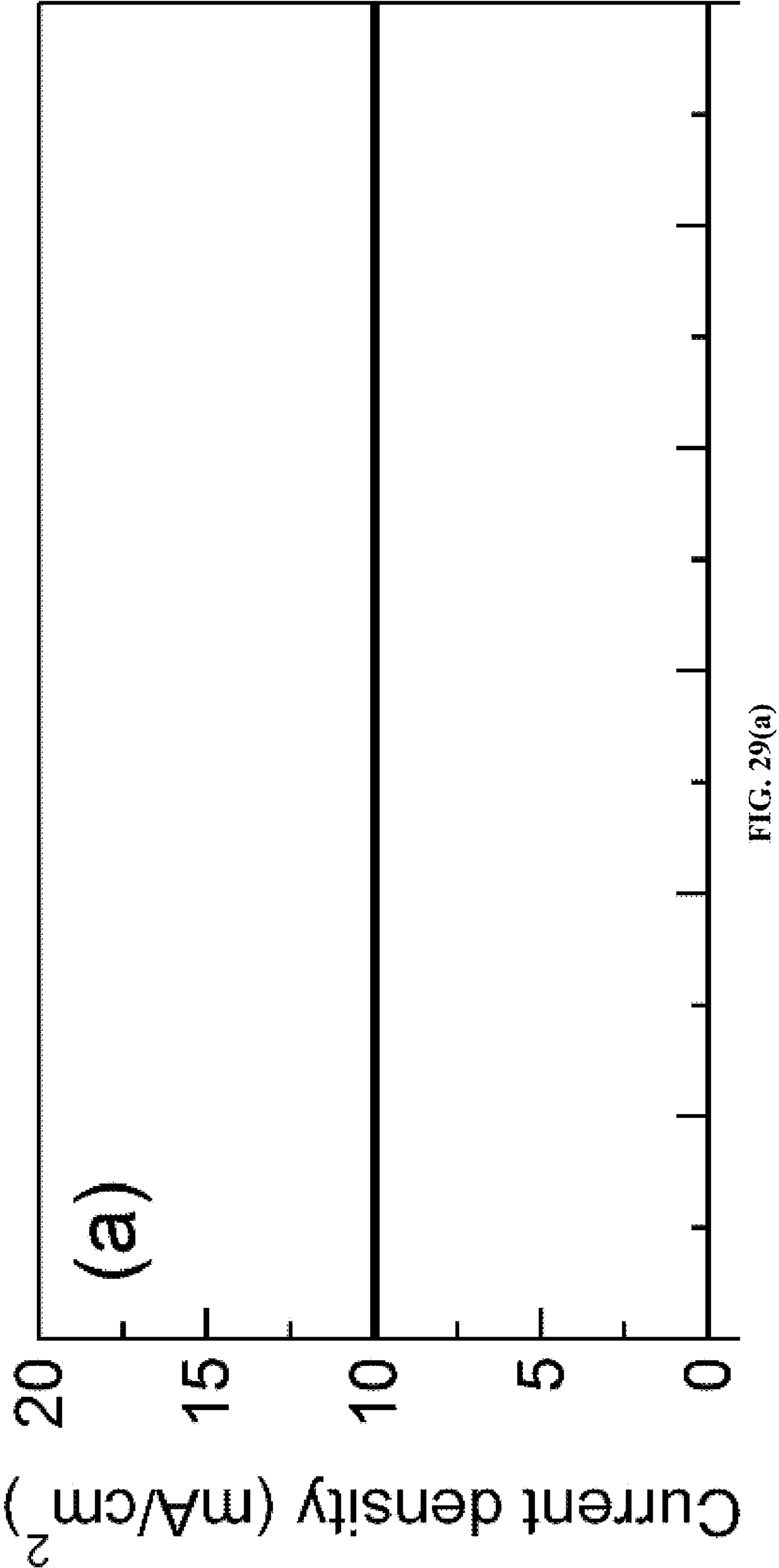


FIG. 28



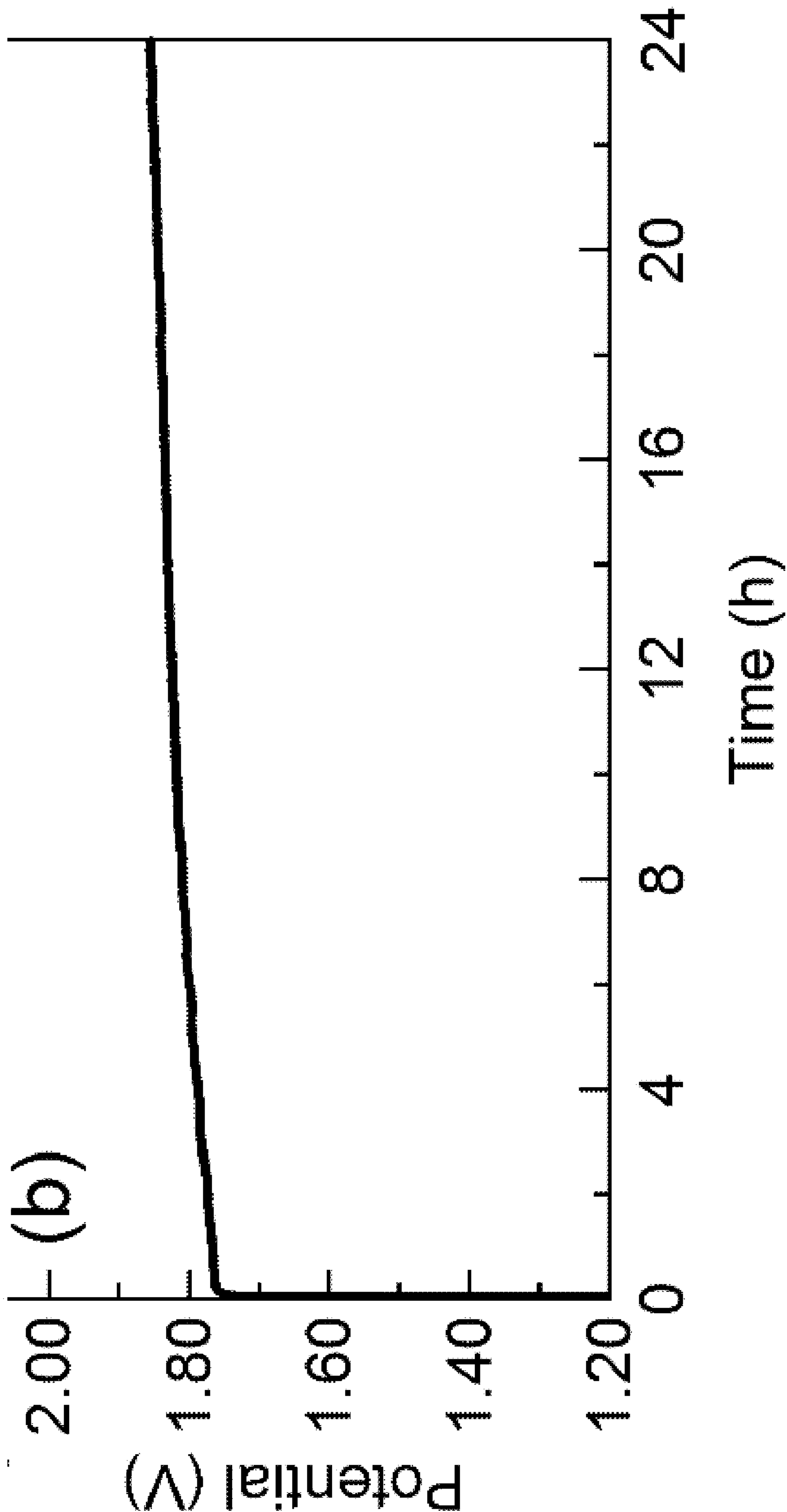


FIG. 29(b)

## BIFUNCTIONAL WATER SPLITTING CATALYSTS AND ASSOCIATED METHODS

### RELATED APPLICATIONS

**[0001]** This application claims priority to U.S. Provisional Patent Application No. 62/141,081, filed on Mar. 31, 2015, the entirety of which is incorporated by reference.

### TECHNICAL FIELD

**[0002]** The present disclosure relates to catalysts and methods for hydrogen and/or oxygen evolution from water. More specifically, it relates to metal-phosphorus-derived film catalysts and methods and applications of the same.

### BACKGROUND

**[0003]** Electrocatalytic water splitting, which consists of  $H_2$  evolution reactions (“HER”) and  $O_2$  evolution reactions (“OER”) has attracted increasing interest in the last few years because of its critical importance in the context of renewable energy research. Most efforts in this field are devoted to developing HER catalysts under strongly acidic conditions for proton-exchange membrane electrolyzers, whereas OER catalysts operate under strongly basic conditions for alkaline electrolyzers. Transition-metal chalcogenides, pnictides, carbides, borides, and even metal-free materials have been reported for HER catalysis in strongly acidic electrolytes. On the other hand, many innovative noble-metal-free OER catalysts based on the oxides/hydroxides of cobalt, nickel, manganese, iron, and copper have also been reported with mediocre to excellent OER catalytic activities under basic conditions.

**[0004]** Despite these advances, challenges for large-scale water splitting catalysis still exist. For instance, to accomplish overall water splitting, it is necessary to integrate both HER and OER catalysts in the same electrolyte. Unfortunately, the current prevailing approaches often lead to inferior overall performance because of the incompatibility of the two types of catalysts functioning under the same conditions. Therefore, it is highly desirable to develop bifunctional and low-cost electrocatalysts that are simultaneously active for both HER and OER in the same electrolyte. Also, ionic conductivity is usually higher at extreme pH values than under neutral conditions and the overpotential loss of OER is much larger than that of HER, plus most OER catalysts are vulnerable in strongly acidic media.

### SUMMARY

**[0005]** The present disclosure in aspects and embodiments addresses these various needs and problems by providing a catalyst, comprising a conductive substrate coated with a metal-phosphorus-derived film, wherein the metal is selected from the group consisting of Manganese, Iron, Cobalt, Nickel, and Copper. In some embodiments, the conductive substrate comprises a material selected from the group consisting of copper, titanium, glassy carbon, fluorine-doped tin oxide, indium-doped tin oxide, tin, nickel, and stainless steel.

**[0006]** Methods for producing the catalysts and for HER and OER are also disclosed herein.

### BRIEF DESCRIPTION OF THE DRAWINGS

**[0007]** The drawings below are supplied in order to facilitate understanding of the Description and Examples provided herein.

**[0008]** FIG. 1 is a graph showing a typical potentiodynamic deposition of a cobalt-phosphorous-derived (“Co—P”) film on a copper foil substrate (scan rate: 5 mV/s).

**[0009]** FIG. 2(a) is an SEM image showing a Co—P film on a Cu foil substrate, with an inset image showing a cross-section of the film. The scale bars for both the SEM image and the inset image are 5  $\mu m$ .

**[0010]** FIG. 2(b) is a high resolution XPS spectra of the Co 2p region of a Co—P film.

**[0011]** FIG. 2(c) is a high resolution XPS spectra of the P 2p region of a Co—P film.

**[0012]** FIG. 3 shows an XPS survey of the as-prepared Co—P film.

**[0013]** FIG. 4(a) is a graph showing the polarization curves of a Co—P film (circles), a platinum-carbon-loaded electrode (“Pt—C”) (dashed) and blank Cu foil (solid line) in 1 M KOH at a scan rate of 2 mV/s and rotating rate of 2,000 rpm. The inset shows the amplified region around the onsets of those polarization curves.

**[0014]** FIG. 4(b) is a graph showing the Tafel plots corresponding to the polarization curves shown in FIG. 4(a) for the Co—P film (solid circles) and Pt—C (open circles). The corresponding linear fittings for each plot are shown in dashed and solid lines, respectively.

**[0015]** FIG. 4(c) is a graph showing the long-term controlled potential electrolysis of a Co—P film (shown in a solid line) and blank Cu foil (shown in a dotted line) in 1 M KOH at an overpotential of 107 mV. The inset is a graph showing the corresponding current change over time of Co—P film (shown in a solid line) and blank Cu foil (shown in a dotted line) during the electrolysis.

**[0016]** FIG. 4(d) is an SEM image of a Co—P film after 2 h of  $H_2$  evolution electrolysis at  $\eta = -107$  mV.

**[0017]** FIG. 5 is an SEM image of the post-HER Co—P film.

**[0018]** FIG. 6(a) shows XPS spectra of the Co 2p regions of a Co—P film after HER electrolysis (top) and after OER electrolysis (bottom).

**[0019]** FIG. 6(b) shows XPS spectra of the P 2p regions of a Co—P film after HER electrolysis (top) and after OER electrolysis (bottom).

**[0020]** FIG. 7(a) shows a cyclic voltammogram of the as-prepared Co—P films before HER electrolysis in the non-Faradaic region.

**[0021]** FIG. 7(b) shows a cyclic voltammogram of the Co—P films after HER electrolysis at  $\eta = -107$  mV in 1 M KOH in the non-Faradaic region.

**[0022]** FIG. 7(c) shows the scan rate dependence of the current densities of the as-prepared and post-HER Co—P films at  $-0.90$  V vs Ag/AgCl.

**[0023]** FIG. 8(a) is a graph showing the polarization curves of a Co—P film (circles), an iridium oxide-loaded electrode (“ $IrO_2$ ”) (dashed line), and blank Cu foil (solid line) in 1 M KOH at scan rate of 2 mV/s and rotating rate of 2000 rpm. The inset shows the amplified region around the onsets of the polarization curves of Co—P/Cu and  $IrO_2$ .

**[0024]** FIG. 8(b) is a graph showing the Tafel plots corresponding to the polarization curves shown in FIG. 4(a) for the Co—P film (circles) and  $IrO_2$  (long dashed line). The

corresponding linear fittings for each plot are shown in short dashed and solid lines, respectively.

[0025] FIG. 8(c) is a graph showing the long-term controlled potential electrolysis of a Co—P film (shown in a solid line) and blank Cu foil (shown in a dotted line) in 1 M KOH at an overpotential of 343 mV. The inset is a graph showing the corresponding current change over time of the Co—P film (shown in a solid line) and blank Cu foil (shown in a dotted line) during the electrolysis.

[0026] FIG. 8(d) is an SEM image of a Co—P film after a 2 h OER electrolysis at  $\eta=343$  mV.

[0027] FIG. 9 shows an XPS survey of the post-OER Co—P film.

[0028] FIG. 10(a) is a graph showing the polarization curves for two electrode (anode/cathode) configurations, including Co—P/Co—P (circles), IrO<sub>2</sub>/Pt—C (long dashed line), Pt—C/Pt—C (short dashed line), and IrO<sub>2</sub>/IrO<sub>2</sub> (solid line) configurations for overall water splitting in 1 M KOH at a scan rate of 2 mV/s. The inset shows the amplified region around the onsets of those polarization curves.

[0029] FIG. 10(b) is a graph showing the Tafel plots corresponding to the polarization curves shown in FIG. 10(a) for the Co—P/Co—P (circles), IrO<sub>2</sub>/Pt—C (long dashed line), Pt—C/Pt—C (short dashed line), and IrO<sub>2</sub>/IrO<sub>2</sub> (solid line) configurations and their associated linear fittings.

[0030] FIG. 10(c) is a graph showing the long-term controlled potential electrolysis of Co—P/Co—P (solid line) and IrO<sub>2</sub>/Pt—C (dashed line) in 1 M KOH. The inset shows the corresponding current change over time of Co—P/Co—P (solid line) and IrO<sub>2</sub>/Pt—C (dashed line).

[0031] FIG. 10(d) is a graph showing the generated H<sub>2</sub> and O<sub>2</sub> volumes over time versus theoretical quantities assuming a 100% Faradaic efficiency for the overall water splitting of Co—P/Co—P in 1 M KOH at  $\eta=400$  mV.

[0032] FIG. 11 is a graph showing a typical potentiodynamic deposition of a nickel-phosphorous-derived (“Co—P”) films on a copper foil substrate (scan rate: 5 mV/s).

[0033] FIG. 12(a) is a graph showing the HER polarizations (1.0 M KOH; scan rate=2 mV/s) of Ni—P films prepared via different potentiodynamic cycles.

[0034] FIG. 12(b) is a graph showing the OER polarizations (1.0 M KOH; scan rate=2 mV/s) of Ni—P films prepared via different potentiodynamic cycles.

[0035] FIG. 13(a) is an SEM image showing a Ni—P film.

[0036] FIG. 13(b) is an SEM image of a cross section of a Ni—P film.

[0037] FIG. 13(c) is a high resolution XPS spectra of the Ni 2p region of an as-prepared Ni—P film, a post-HER Ni—P film and a post OER Ni—P film.

[0038] FIG. 13(d) is a high resolution XPS spectra of the P 2p region of an as-prepared Ni—P film, a post-HER Ni—P film and a post OER Ni—P film.

[0039] FIG. 14 shows XRD patterns of an as-prepared Ni—P film (top) and a blank copper foil (bottom).

[0040] FIG. 15(a) is a graph showing HER polarization curves of Ni—P film, a platinum-carbon-loaded electrode (“Pt—C”), a NiO<sub>x</sub> catalyst film and a blank Cu foil in 1.0 M KOH at a scan rate of 2 mV/s and rotating rate of 2000 rpm. The inset shows the amplified region around the catalytic onsets.

[0041] FIG. 15(b) is a graph showing the Tafel plots corresponding to the polarization curves shown in FIG. 15(a) for the Ni—P film and NiO<sub>x</sub>. The corresponding linear fittings for each plot are shown in dashed lines.

[0042] FIG. 15(c) is a graph showing HER polarization curves for Ni—P film before (solid line) and after (dashed line) 1000 continuous cyclic voltammetric sweeps from 0 to −0.15 V vs RHE in 1.0 M KOH.

[0043] FIG. 15(d) is a representative SEM image of Ni—P film after 2 h controlled potential electrolysis at  $\eta=-110$  mV in 1.0 M KOH.

[0044] FIG. 16 shows controlled potential electrolysis of Ni—P in 1.0 M KOH at an overpotential of −110 mV. The inset shows the corresponding current change over time.

[0045] FIG. 17(a) shows a cyclic voltammogram of the as-prepared Ni—P films before HER electrolysis in the non-Faradaic region.

[0046] FIG. 17(b) shows a cyclic voltammogram of the Ni—P films after HER electrolysis at  $\eta=-110$  mV in 1 M KOH in the non-Faradaic region.

[0047] FIG. 17(c) shows the scan rate dependence of the current densities of the as-prepared and post-HER Ni—P films at −0.85 V vs Ag/AgCl.

[0048] FIG. 18(a) is a graph showing OER polarization curves of Ni—P film, IrO<sub>2</sub>, NiO<sub>x</sub> and blank Cu film in 1.0 M KOH at a scan rate of 2 mV/s and rotating rate of 2000 rpm (the inset shows the amplified region around the catalytic onsets).

[0049] FIG. 18(b) is a graph showing the Tafel plots corresponding to the polarization curves shown in FIG. 17(a) for the Ni—P film, IrO<sub>2</sub>, and NiO<sub>x</sub> with their associated linear fittings (dashed lines).

[0050] FIG. 18(c) is a graph showing OER polarization curves for Ni—P film before (solid line) and after (dashed line) 1000 continuous cyclic voltammetric sweeps from 1.50 to 1.65 V vs RHE in 1.0 M KOH.

[0051] FIG. 18(d) is a representative SEM image of Ni—P film after 2 h controlled potential electrolysis at  $\eta=350$  mV in 1.0 M KOH.

[0052] FIG. 19 is a graph showing OER polarization curves for Ni—P film before (solid line) and after (dashed line) 1,000 continuous cyclic voltammetric sweeps from 1.0 to 1.7 V vs RHE in 1.0 M KOH.

[0053] FIG. 20 shows the Raman spectra of the as-prepared, post-HER, and post-OER samples of Ni—P.

[0054] FIG. 21 is an FTIR spectra of the electrolyte solution (1.0 M KOH) prior to (top) and post (bottom) OER.

[0055] FIG. 22 is a schematic showing an electrical equivalent circuit used to model the Ni—P catalysis system for both HER and OER.

[0056] FIG. 23(a) is a Nyquist plot of Ni—P films for HER under various overpotentials, where the solid lines are corresponding fitting curves. The inset shows the plot of the logarithm  $R_p$  versus overpotential and the corresponding fitting curve.

[0057] FIG. 23(b) is a Nyquist plot of Ni—P films for OER under various overpotentials, where the solid lines are corresponding fitting curves. The inset shows the plot of the logarithm  $R_p$  versus overpotential and the corresponding fitting curve.

[0058] FIG. 24 shows Bode plots of Ni—P for HER.

[0059] FIG. 25 shows Bode plots of Ni—P for OER.

[0060] FIG. 26 shows OER polarization curves (scan rate: 2 mV/s) of Ni—P in KOH of different concentrations.

[0061] FIG. 27(a) is a graph showing Tafel plots of Ni—P film for OER in 1.0 to 5.0 M KOH.

[0062] FIG. 27(b) is a graph showing potentials at current density of 5 and 10 mA/cm<sup>2</sup> versus the logarithm hydroxide anion activity. Dash lines are the corresponding fitting curves.

[0063] FIG. 28 is a graph showing polarization curves (scan rate: 2 mV/s) of a Ni—P/Ni—P catalyst couple for overall water splitting before (solid line) and after (dashed line) 1,000 continuous cyclic voltammetry cycles from 1.5 V to 1.65 V vs RHE in 1.0 M KOH.

[0064] FIG. 29(a) is a graph showing 24 h chronopotentiometry of the Ni—P/Ni—P catalyst couple for overall water splitting in 1.0 M KOH with a current density at 10 mA/cm<sup>2</sup>.

[0065] FIG. 29(b) is a graph showing 24 h chronopotentiometry of the Ni—P/Ni—P catalyst couple for overall water splitting in 1.0 M KOH with potential evolution over time.

#### DETAILED DESCRIPTION

[0066] The present disclosure covers apparatuses and associated methods for the production and related applications of metal-phosphorous-derived films as hydrogen evolution catalysts. In the following description, numerous specific details are provided for a thorough understanding of specific preferred embodiments. However, those skilled in the art will recognize that embodiments can be practiced without one or more of the specific details, or with other methods, components, materials, etc. In some cases, well-known structures, materials, or operations are not shown or described in detail in order to avoid obscuring aspects of the preferred embodiments. Furthermore, the described features, structures, or characteristics may be combined in any suitable manner in a variety of alternative embodiments. Thus, the following more detailed description of the embodiments of the present invention, as illustrated in some aspects in the drawings, is not intended to limit the scope of the invention, but is merely representative of the various embodiments of the invention.

[0067] In this specification and the claims that follow, singular forms such as “a,” “an,” and “the” include plural forms unless the content clearly dictates otherwise. All ranges disclosed herein include, unless specifically indicated, all endpoints and intermediate values. In addition, “optional” or “optionally” refer, for example, to instances in which subsequently described circumstance may or may not occur, and include instances in which the circumstance occurs and instances in which the circumstance does not occur. The terms “one or more” and “at least one” refer, for example, to instances in which one of the subsequently described circumstances occurs, and to instances in which more than one of the subsequently described circumstances occurs.

[0068] The present disclosure covers methods, compositions, reagents, and kits for metal-phosphorus-derived films as competent hydrogen evolution catalysts or oxygen evolution catalysts.

[0069] Aspects of the present disclosure may be further described in Jian, N., You, B, Sheng, M, and Sun, Y., Bifunctionality and Mechanism of Electrodeposited Nickel-Phosphorus Films for Efficient Overall Water Splitting, 8 ChemCatChem 1-6-112 (Dec. 4, 2015) and in Jian, N., You, B, Sheng, M, and Sun, Y., Electrodeposited Cobalt-Phosphorus-Derived Films as Competent Bifunctional Catalysts for Overall Water Splitting, 54 Angew, Chem. Int. Ed.

6251-6254 (Apr. 20, 2015). The entirety of these papers are incorporated herein by reference.

[0070] In embodiments, the catalysts include a conductive substrate coated with a metal-phosphorus-derived film.

[0071] Conductive Substrates:

[0072] Any suitable conductive material capable of being coated with a metal-phosphorus-derived film may be employed in the catalyst. Exemplary conductive substrates include: copper, titanium, glassy carbon, fluorine-doped tin oxide, indium-doped tin oxide, nickel, tin, and stainless steel. Metal foils, such as copper foil may be employed in embodiments where the conductive substrate is a metal.

[0073] Metal-Phosphorus-Derived Film:

[0074] The metal-phosphorus-derived films may use any suitable metal source. Exemplary metals that may be employed in the metal-phosphorus-derived films include: manganese, iron, cobalt, nickel, and copper. In some embodiments, combinations of more than one metal may be used to produce the metal-phosphorus-derived film.

[0075] The metal-phosphorus-derived films may be configured to have a suitable concentration of phosphorus. Exemplary phosphorus/metal ratios include from about 1/20 to about 1/1. In embodiments, phosphorus may be present in the metal-phosphorus-derived films in concentrations, by atomic percentage, of greater than 0 to about 50%, from about 5% to about 50%, from about 5% to about 20%, and about 10%. The ratio of phosphorus to metal may be adjusted depending on the metal being used. For example, in some embodiments employing cobalt as the metal, phosphorous may be present, by atomic percentage, in concentrations of about 5% to about 15%, from about 7% to about 12%, or about 10%. In embodiments employing nickel as the metal, phosphorous may be present, by atomic percentage, in concentrations of about 25% to about 35%, from about 27% to about 32%, or about 30%.

[0076] Any suitable metal source may be employed. In embodiments, affordable metal sources are preferred. Metal chlorides, nitrates, and sulfates salts may be used. For cobalt-phosphorus-derived films, exemplary cobalt sources include cobalt chloride, cobalt sulfate, and cobalt nitrate. For nickel-phosphorus-derived films, exemplary nickel sources include nickel chloride, nickel sulfate, and nickel nitrate. For manganese, iron, and copper-phosphorous-derived films, exemplary metal sources include metal-chlorides, sulfates, and nitrates.

[0077] Any suitable phosphorus source may be used. In embodiments, exemplary phosphorus sources include NaH<sub>2</sub>PO<sub>2</sub>.

[0078] Production Methods:

[0079] Catalysts described in this application may be produced by electrodeposition of the metal-phosphorus-derived film on the conductive substrate. Potentiodynamic deposition methods may be employed to produce catalysts. For example, a NiP film may be readily prepared by potentiodynamic deposition from NiCl<sub>2</sub> and NaH<sub>2</sub>PO<sub>2</sub> in the presence of glycine. In such an embodiment, glycine plays an important role in controlling the deposition potential and rate of the Ni—P film.

[0080] Exemplary films may reach current densities of 10 mAcm<sup>-2</sup> with overpotentials of -93 to -94 mV for HER and 344 to 345 mC for OER with very small Tefel slopes of 42 to 43 and 47 to 49 mV dec<sup>-1</sup>, for HER and OER respectively.

**[0081]** Electrolysis Solutions:

**[0082]** Any suitable electrolysis solution may be used for the production of hydrogen or oxygen. Suitable electrolysis solutions include aqueous solutions comprising a conductive electrolyte. In some embodiments, an alkaline electrolyte or combination thereof, such as KOH or NaOH, may be used in about 1.0 M concentrations. In some embodiments, the electrolysis solution has a pH of from about 7 to about 14, or about 14.

#### EXAMPLES

**[0083]** The following examples are illustrative only and are not intended to limit the disclosure in any way.

##### Example 1

##### Cobalt-Phosphorous-Derived Films

**[0084]** As described in detail below, cobalt-phosphorous-derived (“Co—P”) films were deposited onto a copper foil substrate using a facile potentiodynamic electrodeposition with cobalt and phosphorous reagents. The as-prepared Co—P films can be directly utilized as electrocatalysts for both HER and OER in strong alkaline electrolyte, which can achieve a current density of 10 mA/cm<sup>2</sup> with overpotentials of −94 mV for HER and 345 mV for OER with very small Tafel slopes, 45 and 47 mV/dec, respectively. When the Co—P films were deposited on an anode and cathode for overall water splitting, the superior activity and stability of the catalytic films can even compete versus the integrated Pt and IrO<sub>2</sub> catalyst couple.

**[0085]** Materials

**[0086]** Cobalt sulfate, sodium acetate, sodium hypophosphite monohydrate, potassium hydroxide were purchased from commercial vendors and used as received. Pt—C (20% Pt on Vulcan XC-72) and iridium (IV) oxide were purchased from Premetek Co. and Alfa Aesa, respectively, and used as received. Nafion 117 solution (5% in a mixture of lower aliphatic alcohols and water) was purchased from Sigma-Aldrich. Copper foils (3M™ copper conductive tapes, single adhesive surface) were purchased from Ted Pella, Inc. Water was deionized (18Ω) with a Barnstead E-Pure system.

**[0087]** Electrochemical Methods

**[0088]** Electrochemical experiments were performed on Gamry Interface 1000 potentiostats. Aqueous Ag/AgCl reference electrodes (saturated KCl) were purchased from CH Instruments. The reference electrode in aqueous media was calibrated with ferrocenecarboxylic acid whose Fe<sup>3+/2+</sup> couple is 0.284 V vs SCE. All potentials reported in this paper were converted from vs Ag/AgCl to vs RHE by adding a value of 0.197+0.059×pH to vs RHE. iR (current times internal resistance) compensation was applied in polarization and controlled potential electrolysis experiments to account for the voltage drop between the reference and working electrodes using the Gamary Framework™ Data Acquisition Software 6.11.

**[0089]** Preparation of Co—P Films

**[0090]** Prior to electrodeposition, copper foils were rinsed with water and ethanol thoroughly to remove residual organic species. For linear sweep voltammetry experiments, a circular copper foil with a 3 mm diameter was prepared and pasted on the rotating disk glassy carbon electrode, then the assembled electrode was exposed to the deposition solution (50 mM CoSO<sub>4</sub>, 0.5 M NaH<sub>2</sub>PO<sub>2</sub>, and 0.1 M

NaOAc in water). A platinum wire was used as the counter electrode and a Ag/AgCl (sat. KCl) electrode as the reference electrode. Nitrogen was bubbled through the electrolyte solution for at least 20 min prior to deposition and maintained during the entire deposition process. The potential of consecutive linear scans was cycled 15 times between −0.3 and −1.0 V vs Ag/AgCl at a scan rate of 5 mV/s under stirring and a rotation rate of 500 rpm. After deposition, the assembled electrode was removed from the deposition bath and rinsed with copious water gently. The prepared Co—P film can be directly used to collect its polarization curves or stored under vacuum at room temperature for future use. For samples prepared for controlled potential electrolysis, a copper foil was directly used the working electrode with a geometric area of 0.3 cm<sup>2</sup> exposed to the electrolyte. The deposition potential window and cycle number are the same as aforementioned. Typical potentiodynamic depositions of Co—P films are shown in FIG. 1.

**[0091]** Preparation of Pt—C and IrO<sub>2</sub>-Loaded Electrodes

**[0092]** 12 mg Pt—C or IrO<sub>2</sub> were dispersed in a 2 mL mixture solution containing 800 μL water, 120 μL 5% Nafion solution, and 1.08 mL ethanol, followed by sonication for 30 min to obtain a homogeneous catalyst ink. 2 μL catalyst ink was loaded on the surface of a glassy carbon electrode (surface area: 0.07065 cm<sup>2</sup>) for 6 times. Consequently, the overall loading amount is 1 mg/cm<sup>2</sup>.

**[0093]** Physical Methods

**[0094]** Scanning electron microscopy images and elemental mapping analysis were collected on a FEI QUANTA FEG 650 (FEI, USA) by FenAnn Shen at the Microscopy Core Facility of USU. Cobalt and phosphorous analysis were obtained on a Thermo Electron iCAP inductively coupled plasma spectrophotometer at the Analytical Laboratory of USU. X-ray photoelectron spectroscopy analyses were done using a Kratos Axis Ultra instrument (Chestnut Ridge, N.Y.) at Surface Analysis and Nanoscale Imaging group at the University of Utah, sponsored by the College of Engineering, Health Sciences Center, Office of the Vice President for Research, and the Utah Science Technology and Research (USTAR) Initiative of the State of Utah. The samples were affixed on a stainless steel Kratos sample bar, loaded into the instrument's load lock chamber, and evacuated to 5×10<sup>−8</sup> torr before it was transferred into the sample analysis chamber under ultrahigh vacuum conditions (~10<sup>−10</sup> torr). X-ray photoelectron spectra were taken using the monochromatic Al Kα source (1486.7 eV) at a 300×700 μm spot size. Low resolution survey and high resolution region scans at the binding energy of interest were taken for each sample. To minimize charging, samples were flooded with low-energy electrons and ions from the instrument's built-in charge neutralizer. The samples were also sputter cleaned inside the analysis chamber with 1 keV Ar<sup>+</sup> ions for 30 seconds to remove adventitious contaminants and surface oxides. Data were analyzed using CASA XPS software, and energy corrections on high resolution scans were done by referencing the C1s peak of adventitious carbon to 284.5 eV. This work also made use of the Surface Analysis and Nanoscale Imaging group at the University of Utah. The generated hydrogen volume during electrolysis was quantified with a SRI gas chromatography system 8610C equipped with a Molecular Sieve 13× packed column, a HayesSep D packed column, and a thermal conductivity detector. The oven temperature was maintained at 60° C. and argon was used as the carrier gas.

**[0095]** Results

**[0096]** Cobalt-phosphorous-derived (“Co—P”) films were deposited onto a copper foil substrate using a facile potentiodynamic electrodeposition with cobalt and phosphorous reagents. FIG. 1 shows a typical potentiodynamic deposition of Co—P films on a copper foil substrate (scan rate: 5 mV/s). Scanning electron microscopy (SEM) images of the as-prepared Co—P film show nearly complete coverage of the rough film on copper foil (FIG. 2(a)), with no observed crystalline particles or aggregates. Elemental mapping analysis indicated Co and P were distributed evenly over the entire film (data not shown). The cross section SEM image reveals the thickness of the film is about 1-3  $\mu\text{m}$  (FIG. 2(a) inset). The X-ray photoelectron spectroscopy (XPS) survey of the as-prepared film (FIG. 3) shows all the anticipated elements. The Co 2p XPS spectrum (FIG. 2(b)) displays two peaks at 778.3 and 793.4 eV, corresponding to the Co 2p<sub>3/2</sub> and 2p<sub>1/2</sub> binding energies, respectively. These values are extremely close to those of metallic cobalt. The P 2p XPS spectrum (FIG. 2(c)) exhibits a dominant peak at 129.5 eV, which can be attributed to the phosphide signal. A broad feature at  $\sim$ 133.6 eV is assigned to phosphate. In addition, as shown in Table 1 below, elemental analysis of the as-prepared Co—P film measured the amount of Co and P as 2.52 and 0.19 mg/cm<sup>2</sup>, respectively, with a molar ratio of about 6.98.

TABLE 1

| ICP-OES data of as-prepared Co—P film, and of Co—P film after 2 h HER electrolysis and after 2 h OER electrolysis. |                         |                            |                           |                 |
|--------------------------------------------------------------------------------------------------------------------|-------------------------|----------------------------|---------------------------|-----------------|
| Sample                                                                                                             | Area (cm <sup>2</sup> ) | [Co] (mg/cm <sup>2</sup> ) | [P] (mg/cm <sup>2</sup> ) | Co/P mole ratio |
| Fresh prepared                                                                                                     | 0.3                     | 2.52                       | 0.19                      | 6.98            |
| After 2 h HER electrolysis                                                                                         | 0.3                     | 2.48                       | 0.12                      | 10.5            |
| After 2 h OER electrolysis                                                                                         | 0.3                     | 2.47                       | 0.13                      | 9.74            |

**[0097]** We first evaluated the HER activity of a Co—P film in strong alkaline solution (See FIGS. 4(a)-4(d)), by comparing the performance of the Co—P film to a platinum-carbon-loaded electrode (“Pt—C”) and blank Cu foil. The blank copper foil did not show any HER catalytic activity before  $-0.3$  V vs a reversible hydrogen electrode (“RHE”) (See FIG. 4(a)). In contrast, a rapid cathodic current rise was observed for the Co—P film beyond  $-50$  mV vs RHE (FIG. 4(a) inset). Further scanning towards negative potential produced a dramatic increase in current density along with vigorous evolution of H<sub>2</sub> bubbles from the electrode surface. The Co—P film required an overpotential ( $\eta$ ) of only  $-94$  mV to reach a current density of 10 mA/cm<sup>2</sup>. As shown in Table 2, such a low overpotential requirement compares favorably to other reported HER catalysts at pH 14:

TABLE 2

| Comparison of selected nonprecious HER electrocatalysts in alkaline media. |             |                          |             |                                    |           |
|----------------------------------------------------------------------------|-------------|--------------------------|-------------|------------------------------------|-----------|
| Catalysts                                                                  | Electrolyte | j (mA cm <sup>-2</sup> ) | $\eta$ (mV) | Tafel slop (mV dec <sup>-1</sup> ) | Reference |
| Co—P film                                                                  | 1M          | 10                       | 94          | 42                                 | This work |
|                                                                            | KOH         | 20                       | 115         |                                    |           |
|                                                                            |             | 100                      | 158         |                                    |           |

TABLE 2-continued

| Comparison of selected nonprecious HER electrocatalysts in alkaline media. |             |                          |             |                                    |                                               |
|----------------------------------------------------------------------------|-------------|--------------------------|-------------|------------------------------------|-----------------------------------------------|
| Catalysts                                                                  | Electrolyte | j (mA cm <sup>-2</sup> ) | $\eta$ (mV) | Tafel slop (mV dec <sup>-1</sup> ) | Reference                                     |
| CoP/CC                                                                     | 1M KOH      | 10                       | 209         | 129                                | <i>J. Am. Chem. Soc.</i> 2014, 136, 7587      |
| Co—S/FTO                                                                   | 1M KOH      | 1                        | 480         | N/A                                | <i>J. Am. Chem. Soc.</i> 2013, 135, 17699     |
| Co—NRCNTs                                                                  | 1M KOH      | 10                       | 370         | N/A                                | <i>Angew. Chem. Int. Ed.</i> 2014, 53, 4372.  |
| Ni <sub>2</sub> P                                                          | 1M KOH      | 20                       | 205         | N/A                                | <i>J. Am. Chem. Soc.</i> 2013, 135, 9267.     |
| Ni/Ni(OH) <sub>2</sub>                                                     | 0.1M KOH    | 10                       | >300        | 128                                | <i>Angew. Chem. Int. Ed.</i> 2012, 51, 12495. |
| MoB                                                                        | 0.1M KOH    | 10                       | 225         | 59                                 | <i>Angew. Chem. Int. Ed.</i> 2012, 51, 12703. |
| MoS <sub>2+x</sub> /FTO                                                    | 1M KOH      | 10                       | 310         | N/A                                | <i>Angew. Chem. Int. Ed.</i> 2015, 54, 667.   |
| Amorphous MoS <sub>x</sub>                                                 | 0.1M KOH    | 10                       | 540         | N/A                                | <i>Chem. Sci.</i> 2011, 2, 1262.              |
| FeP                                                                        | 1M KOH      | 10                       | 218         | 146                                | <i>ACS Catal.</i> 2014, 4, 4065.              |
| NAs/CC                                                                     | KOH         |                          |             |                                    |                                               |

**[0098]** Remarkably, the Co—P film was able to produce a catalytic current density of 1000 mA/cm<sup>2</sup> within an overpotential of  $-227$  mV. The linear fitting of its Tafel plot (FIG. 4(b)) rendered a Tafel slope of 42 mV/dec, which is among the smallest Tafel slopes of reported HER catalysts in alkaline media (See Table 2). Although Pt—C exhibited a very small catalytic onset potential, its Tafel slope (108 mV/dec) was significantly larger than that of the Co—P film (FIG. 4(b)). Therefore, beyond  $-167$  mV vs RHE, the catalytic current density of Co—P surpassed that of Pt—C. Additionally, the Co—P film also exhibited superior long-term stability. A 24 h controlled potential electrolysis at  $\eta = -107$  mV showed a nearly linear charge accumulation and steady current over the entire course of electrolysis (FIG. 4(c)). The blank copper foil only generated negligible charge build-up under the same condition.

**[0099]** To probe the morphology and composition of the Co—P film after HER electrocatalysis, the SEM and XPS results of a post-HER Co—P film were collected. As shown in FIG. 4(d), the film still maintained a uniform coverage on the copper foil and no apparent clusters or aggregates were observed (FIG. 5). Elemental mapping analysis confirmed the even distribution of Co and P in the post-HER film (data not shown). The Co 2p XPS spectrum of the Co—P film after HER electrolysis shows two peaks at 793.2 and 778.2 eV (FIG. 6(a), top), corresponding to Co 2p<sub>3/2</sub> and 2p<sub>1/2</sub> states, respectively. The similarity of the Co 2p peaks of the post-HER Co—P film compared to those of the as-prepared Co—P film (FIG. 2b) implies the major composition of the film preserved as metallic cobalt during HER. Further, a peak at 129.3 eV was observed from the P 2p XPS spectrum of the post-HER sample (FIG. 6(b), top); while the phosphate peak at 133.6 eV originally observed for the as-prepared Co—P film (FIG. 2(c)) was absent. Its absence is likely due to the dissolution of cobalt phosphate under cathodic condition. As shown in FIG. 7(a)-7(c), the as-prepared and post-HER Co—P films exhibited similar capacitance, implying their similar electrical active surface

area. Elemental analysis of the post-HER film resulted in Co and P amount of 2.48 and 0.12 mg/cm<sup>2</sup> with a Co/P ratio of 10.5 (See Table 1 above).

**[0100]** We next assessed the catalytic activity of the Co—P film for OER in the same electrolyte (See FIGS. 8(a)-8(d)), by comparing the performance of the Co—P film to an iridium oxide-loaded electrode (“IrO<sub>2</sub>”) and blank Cu foil (“Blank”). As expected, a blank copper foil did not show appreciable anodic current before 1.7 V vs RHE (FIG. 8(a)). The OER catalytic current density of the Co—P film increased dramatically beyond 1.53 V vs RHE (FIG. 8a, inset). It could reach current densities of 10, 100, and 500 mA/cm<sup>2</sup> at  $\eta$ =345, 413, and 463 mV, respectively, lower than those of IrO<sub>2</sub> and many other reported OER catalysts, as shown in Table 3:

TABLE 3

| Comparison of selected nonprecious OER electrocatalysts in alkaline media. |              |                                                |                                              |                                                 |
|----------------------------------------------------------------------------|--------------|------------------------------------------------|----------------------------------------------|-------------------------------------------------|
| Catalysts                                                                  | Electrolyte  | $\eta$<br>(mV) at<br>10 mA<br>cm <sup>-2</sup> | Tafel<br>slope<br>(mV<br>dec <sup>-1</sup> ) | Reference                                       |
| Co—P film                                                                  | 1.0M<br>KOH  | 345                                            | 47                                           | This work                                       |
| NiCo LDH                                                                   | 1.0M<br>KOH  | 367                                            | 40                                           | <i>Nano Lett.</i><br>2015, 15, 1421.            |
| Cu—N—C/<br>graphene                                                        | 0.1M<br>KOH  | >770                                           | N/A                                          | <i>Nat. Commun.</i><br>2014, 5, 5285.           |
| CoCo LDH                                                                   | 1.0M<br>KOH  | 393                                            | 59                                           | <i>Nat. Commun.</i><br>2014, 5, 4477.           |
| Co <sub>3</sub> O <sub>4</sub> /rm-GO                                      | 1.0M<br>KOH  | 310                                            | 67                                           | <i>Nat. Mater.</i><br>2011, 10, 780.            |
| MnO <sub>x</sub> /Au                                                       | 0.1M<br>KOH  | >480                                           | N/A                                          | <i>J. Am. Chem. Soc.</i><br>2014, 136, 4920.    |
| Ca <sub>2</sub> Mn <sub>2</sub> O <sub>5</sub> /C                          | 0.1M<br>KOH  | >470                                           | 149                                          | <i>J. Am. Chem. Soc.</i><br>2014, 136, 14646.   |
| Co <sub>x</sub> O <sub>y</sub> /NC                                         | 0.1M<br>KOH  | 430                                            | N/A                                          | <i>Angew. Chem. Int. Ed.</i><br>2014, 53, 8508. |
| De-LiCoO <sub>2</sub>                                                      | 0.1M<br>KOH  | >400                                           | 50                                           | <i>Nat. Commun.</i><br>2014, 5, 4345.           |
| CoMn LDH                                                                   | 1.0M<br>KOH  | 324                                            | 43                                           | <i>J. Am. Chem. Soc.</i><br>2014, 136, 16481.   |
| NiFeOx film                                                                | 1.0M<br>NaOH | >350                                           | N/A                                          | <i>J. Am. Chem. Soc.</i><br>2013, 135, 16977.   |
| CoO/NG                                                                     | 1.0M<br>KOH  | 340                                            | 71                                           | <i>Energy Environ. Sci.</i><br>2014, 7, 609.    |
| CoO <sub>x</sub> film                                                      | 1.0M<br>KOH  | 403                                            | 42                                           | <i>J. Am. Chem. Soc.</i><br>2012, 134, 17253.   |
| $\alpha$ -MnO <sub>2</sub> —SF                                             | 0.1M<br>KOH  | 490                                            | 77.5                                         | <i>J. Am. Chem. Soc.</i><br>2014, 136, 11452.   |
| MnO <sub>x</sub> film                                                      | 1.0M<br>KOH  | 563                                            | 49                                           | <i>J. Am. Chem. Soc.</i><br>2012, 134, 17253.   |
| NiFeO <sub>x</sub> film                                                    | 1.0M<br>NaOH | >350                                           | N/A                                          | <i>J. Am. Chem. Soc.</i><br>2013, 135, 16977.   |
| Fe—Ni oxides                                                               | 1.0M<br>KOH  | >375                                           | 51                                           | <i>ACS Catal.</i><br>2012, 2, 1793.             |
| Zn <sub>x</sub> Co <sub>3-x</sub> O <sub>4</sub><br>nanowire               | 1.0M<br>KOH  | 330                                            | 51                                           | <i>Chem. Mater.</i><br>2014, 26, 1889.          |
| Ni <sub>x</sub> Co <sub>3-x</sub> O <sub>4</sub><br>nanowire               | 1.0M<br>KOH  | ~370                                           | 59-64                                        | <i>Adv. Mater.</i><br>2010, 22, 1926.           |

Linear fitting of its Tafel plot resulted in a Tafel slope of 47 mV/dec (FIG. 8(b)). As one of the state-of-the-art OER catalysts, IrO<sub>2</sub> was able to catalyze OER at a lower onset of ~1.50 V vs RHE. However, its performance was quickly exceeded by that of the Co—P film beyond 1.58 V vs RHE. In fact, the Tafel slope of Co—P (47 mV/dec) is even lower than that of IrO<sub>2</sub> (55 mV/dec), demonstrating more favorable OER kinetics of the former. Besides high OER activity,

the Co—P film also features excellent stability, as revealed by a 24 h controlled potential electrolysis at  $\eta$ =343 mV (FIG. 8(c)).

**[0101]** The SEM image of the post-OER Co—P film (FIG. 8(d)) indicates it contains large nanoparticle aggregates, in sharp contrast to the rough and porous morphology of the as-prepared and post-HER samples. Nevertheless, elemental mapping analysis still demonstrated an even distribution of Co and P in the film (data not shown), plus a large concentration of O. Indeed, an intense O is peak was observed in the XPS survey spectrum of the post-OER film (FIG. 9). The Co 2p spectrum displayed two peaks at 780.7 and 796.3 eV (FIG. 6(a), bottom), which can be assigned to oxidized cobalt, Co<sub>3</sub>O<sub>4</sub>, plus its satellite peaks at 786.3 and 802.7 eV. However, the metallic cobalt 2p peaks at 778.0 and 793.0 eV could still be well resolved. The P 2p spectrum showed a phosphate peak at 133.2 eV (FIG. 6(b)), whereas the original phosphide feature at 129.5 eV disappeared completely. Taken together, it indicates that the original cobalt in the Co—P film was partially oxidized to Co<sub>3</sub>O<sub>4</sub> and cobalt phosphate during OER. An OER electrocatalyst with a metallic cobalt core and cobalt oxide/hydroxide shell was reported. Elemental analysis of the post-OER film resulted in the remaining amount of Co and P as 2.47 and 0.13 mg/cm<sup>2</sup> with a Co/P ratio of 9.74 (See Table 1), still similar to those of the post-HER film.

**[0102]** Based on the results aforementioned, we anticipated that the Co—P film could act as a bifunctional electrocatalyst for overall water splitting. Hence, a two-electrode configuration was employed, with Co—P and on Cu substrates were used as both the anode and the cathode (i.e., Co—P/Co—P). The performance of the Co—P/Co—P configurations were compared to the performance of IrO<sub>2</sub>/Pt—C, Pt—C/Pt—C, and IrO<sub>2</sub>/IrO<sub>2</sub> configurations (see FIGS. 10(a)-10(d)). When the as-prepared Co—P films were used as electrocatalysts for both anode and cathode (Co—P/Co—P couple), a catalytic current was observed when the applied potential was larger than 1.56 V with a Tafel slope of 69 mV/dec.

**[0103]** The rapid catalytic current density exceeded 100 mA/cm<sup>2</sup> at 1.744 V. When Pt—C or IrO<sub>2</sub> was used for both electrodes (Pt—C/Pt—C or IrO<sub>2</sub>/IrO<sub>2</sub> couple), much diminished catalytic current densities were obtained with large Tafel slopes of 166 and 290 mV/dec, respectively. Since Pt is well-known for HER and IrO<sub>2</sub> for OER, the integration of Pt—C on cathode and IrO<sub>2</sub> on anode was expected to produce an excellent catalytic system. Indeed, the IrO<sub>2</sub>/Pt—C couple was able to catalyze water splitting with an onset around 1.47 V (FIG. 10(a), inset). However, the Tafel slope of IrO<sub>2</sub>/Pt—C is 91 mV/dec, larger than that of Co—P/Co—P (69 mV/dec). Therefore, when the applied potential was higher than 1.67 V, Co—P/Co—P was able to surpass IrO<sub>2</sub>/Pt—C in catalyzing overall water splitting. In addition, the Co—P/Co—P couple maintained excellent stability as manifested by the steady current change and nearly linear charge accumulation for a 24 h electrolysis (FIG. 10(c)). In fact, the integrated activity of IrO<sub>2</sub>/Pt—C was slightly inferior to that of the Co—P/Co—P couple under the same condition. FIG. 10(d) shows the produced H<sub>2</sub> and O<sub>2</sub> quantified by gas chromatography match the calculated amount based on passed charge well and the volume ratio of H<sub>2</sub> and O<sub>2</sub> is close to 2, leading to a Faradaic efficiency of 100%.

**[0104]** In conclusion, we have reported electrodeposited Co—P films can act as bifunctional catalysts for overall water splitting. The catalytic activity of the Co—P films can rival the state-of-the-art catalysts, requiring  $\eta = -94$  mV for HER and  $\eta = 345$  mV for OER to reach  $10 \text{ mA/cm}^2$  with Tafel slopes of 45 and 47 mV/dec, respectively. It can be directly utilized as catalysts for both anode and cathode with superior efficiency, strong robustness, and 100% Faradaic yield. The understanding of real-time composition and structural evolution of the film during electrolysis requires in situ spectroscopic study, which is under current investigation.

## Example 2

### Nickel-Phosphorous-Derived Films

**[0105]** As described in detail below, nickel-phosphorous-derived (“Ni—P”) films were deposited onto a copper foil substrate using a facile potentiodynamic electrodeposition with cobalt and phosphorous reagents. The as-prepared Ni—P films can be directly utilized as electrocatalysts for both HER and OER in strong alkaline electrolyte, (1.0 M KOH).

#### **[0106]** Materials

**[0107]** Nickel chloride hexahydrate ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ), glycine, sodium hypophosphite monohydrate ( $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ ), sodium acetate (NaOAc), and potassium hydroxide (KOH) were all purchased from commercial vendors and used directly without any further purification. Nafion 117 solution (5% in a mixture of lower aliphatic alcohols and water) was purchased from Sigma-Aldrich. Copper foils (3M™ copper conductive tapes, single adhesive surface) were purchased from Ted Pella, Inc. Water was deionized (18 MQ) using a Barnstead E-Pure system.

#### **[0108]** Preparation of Catalyst Films (Ni—P and $\text{NiO}_x$ )

**[0109]** Prior to electrodeposition, copper foils were rinsed with water and ethanol thoroughly to remove residual organic species. For linear sweep voltammetry experiments, a circular copper foil with a 3 mm diameter was prepared and pasted on the rotating disk glassy carbon electrode, and then the assembled electrode was exposed to the optimized deposition solution (50 mM  $\text{NiCl}_2$ , 1 M  $\text{NaH}_2\text{PO}_2$ , 0.16 M glycine, and 0.1 M NaOAc in water). A platinum wire was used as the counter electrode and a Ag/AgCl (sat. KCl) electrode as the reference electrode. Nitrogen was bubbled through the electrolyte solution for at least 20 min prior to deposition and maintained during the entire deposition process. The potential of consecutive linear scans was cycled between 0.1 and  $-1.1$  V vs Ag/AgCl at a scan rate of 5 mV/s and a rotation rate of 500 rpm (FIG. 11). After deposition, the working electrode was rinsed with water and acetone gently and dried under vacuum at room temperature, followed by direct use for electrocatalysis.

**[0110]** The HER and OER polarization curves of Ni—P films prepared via potentiodynamic deposition cycles of 5, 10, 15, and 20 are compared in FIGS. 12(a) and 12(b). It is apparent that the cycle number of 15 produced a Ni—P film with the best HER and OER electrocatalytic activities. Hence, all the electrochemical experiments discussed in the main text were conducted using the Ni—P films prepared via 15 cycles.

**[0111]** The control  $\text{NiO}_x$  catalyst films were prepared according to a reported method (*J. Phy. Chem. C* 2014, 118, 4578-4584, the complete disclosure of which is herein incorporated by reference in its entirety). Briefly, a copper

foil with an exposed area of  $0.3 \text{ cm}^2$  was used as the working electrode with platinum wire and Ag/AgCl (sat. KCl) as the counter and reference electrodes, respectively. 10 mL 0.1 M NaBi with 1.0 mM  $\text{Ni}(\text{NO}_3)_2$  was used as the electrolyte. Prior to electrodeposition, the copper foil was rinsed with acetone and deionized water thoroughly. Electrolysis was carried out at  $-1.2$  V vs Ag/AgCl for three hours under deaerated condition.

#### **[0112]** Preparation of Pt—C and $\text{IrO}_2$ -Loaded Electrodes

**[0113]** 12 mg Pt—C or  $\text{IrO}_2$  was dispersed in a 2 mL mixture solution containing 800  $\mu\text{L}$  water, 120  $\mu\text{L}$  5% Nafion solution, and 1.08 mL ethanol, followed by sonication for 30 min to obtain a homogeneous catalyst ink. 3  $\mu\text{L}$  catalyst ink was loaded on the surface of a glassy carbon electrode (surface area:  $0.07065 \text{ cm}^2$ ) for 6 times. Consequently, the overall loading amount is  $1.53 \text{ mg/cm}^2$ .

#### **[0114]** Catalyst Characterization

**[0115]** Powder X-ray diffractions were recorded on a Rigaku MiniflexII Desktop X-ray diffractometer. Scanning electron microscopy (SEM) images were collected on a FEI QUANTA FEG 650 (FEI, USA). Elemental analysis of nickel and sulfur was obtained on a Thermo Electron iCAP inductively coupled plasma spectrophotometer. Fourier transform infrared (FTIR) spectroscopy was conducted on an IR100 Spectrometer (Thermo Nicolet). The Raman spectra were recorded with a confocal Raman microspectrometer (Renishaw, U.K.) under a 785 nm diode laser excitation. The detection of the Raman signal was carried out with a Peltier cooled charge-coupled device (CCD) camera. The software package WIRE 3.0 (Renishaw) was employed for spectral acquisition and analysis. X-ray photoelectron spectroscopy analyses were conducted on a Kratos Axis Ultra instrument (Chestnut Ridge, N.Y.). The samples were affixed on a stainless steel Kratos sample bar, loaded into the instrument's load lock chamber, and evacuated to  $5 \times 10^{-8}$  torr before it was transferred into the sample analysis chamber under ultrahigh vacuum conditions ( $\sim 10^{-10}$  torr). X-ray photoelectron spectra were taken using the monochromatic Al  $K\alpha$  source (1486.7 eV) at a  $300 \times 700 \mu\text{m}$  spot size. High resolution region scans at the binding energies of interest were taken for each sample. To minimize charging, samples were flooded with low-energy electrons and ions from the instrument's built-in charge neutralizer. The samples were first sputter cleaned inside the analysis chamber with 1 keV  $\text{Ar}^+$  ions for 30 seconds to remove adventitious contaminants and surface oxides. Data were analyzed using Casa-XPS software, and energy corrections on high resolution scans were calibrated by referencing the C1s peak of adventitious carbon to 284.5 eV.

#### **[0116]** Electrochemical Measurements

**[0117]** Electrochemical experiments were performed on a Gamry Interface 1000 potentiostat workstation with a three-electrode cell system. The as-prepared Ni—P ( $d = 3 \text{ mm}$ ,  $S = 0.07065 \text{ cm}^2$ ) was used as the working electrode, a Ag/AgCl (sat. KCl) electrode (CH Instruments) as the reference electrode, and a platinum wire as the counter electrode. All potentials reported in the paper were converted to vs RHE (reversible hydrogen electrode) by adding a value of  $0.197 + 0.059 \times \text{pH}$  to vs RHE. iR (current times internal resistance) correction was applied for linear sweep voltammetry and controlled potential electrolysis experiments to account for the voltage drop between the reference and working electrodes using Gamry Framework™ Data Acquisition Software 6.11. The linear sweep voltammetry

experiments were conducted in N<sub>2</sub> saturated 1.0 M KOH electrolyte at a scan rate of 2 mV/s and a rotating speed of 2000 rpm. Electric impedance spectroscopy measurements in deaerated 1.0 M KOH were carried out in the same configuration at multiple potentials from 10<sup>5</sup> to 0.1 Hz with an AC potential amplitude of 30 mV.

#### [0118] Results

**[0119]** The Ni—P film can be readily prepared via potentiodynamic deposition from NiCl<sub>2</sub> and NaH<sub>2</sub>PO<sub>2</sub> in the presence of glycine (FIG. 11). It is noted that glycine plays an important role in controlling the deposition potential and rate of the Ni—P film. The Ni—P films are able to reach a current density of 10 mA/cm<sup>2</sup> with overpotentials of −93 mV for HER and 344 mV for OER with very small Tafel slopes of 43 and 49 mV/dec, respectively, rivaling the performance of the state-of-the-art HER and OER catalysts, Pt and IrO<sub>2</sub>, respectively. Mechanistic studies revealed that the catalytic rate of OER was first order in the activity of hydroxide anion. Even more appealing is that when the Ni—P films are deposited on the anode and cathode for overall water splitting, excellent activity and stability for overall water splitting can be achieved. Overall, the low-cost, efficient, robust, and bifunctional nature of the Ni—P film renders it a competent catalyst for overall water splitting.

**[0120]** The scanning electron microscopy (SEM) image of an as-prepared Ni—P film is shown in FIG. 13(a), exhibiting nearly complete coverage of the rough film on a copper foil. The black holes in the film are potentially due to the formation of H<sub>2</sub> bubbles during the deposition of the film under negative potentials. The cross section SEM image (FIG. 13(b)) reveals the thickness of the film is around 3 μm. The elemental mapping results of Ni—P confirm the presence of nickel and phosphorous which are homogeneously distributed over the entire film (data not shown). Its powder X-ray diffraction (XRD) pattern is almost identical to that of a blank copper foil with no unique feature that can be attributed to the Ni—P film (FIG. 14). Therefore, the Ni—P film is amorphous in nature. We further conducted X-ray photoelectron spectroscopy (XPS) to probe the valence states of nickel and phosphorous in the film. As shown in FIG. 13(c), the high-resolution Ni 2p XPS spectrum displays two peaks at 853.0 and 870.3 eV, corresponding to the Ni 2p<sub>3/2</sub> and 2p<sub>1/2</sub> binding energies, respectively. These value are quite close to those of metallic nickel. The high-resolution P 2p spectrum (FIG. 13(d)) exhibits a dominant feature in the region of 129 to 131 eV, which can be assigned to the anticipated phosphide signal. Elemental analysis via inductively coupled plasma optical emission spectrometry of the as-prepared Ni—P samples implied the deposited amounts of nickel and phosphorous as 1.30 and 0.35 mg/cm<sup>2</sup>, resulting in a Ni/P atomic ratio close to 2.

**[0121]** The electrocatalytic activity of Ni—P was first evaluated for H<sub>2</sub> evolution in a strongly alkaline electrolyte (1.0 M KOH), as shown in FIGS. 15(a)-15(d). A blank copper foil, commercially available 20 wt % Pt—C(Pt—C), and nickel oxide (NiO<sub>x</sub>) electrodeposited on copper foil following a reported method (C. He, X. Wu, Z. He, *J. Phys. Chem. C* 2014, 118, 4578-4584) were also included as comparisons. The blank copper foil did not exhibit appreciable HER activity, with nearly no catalytic current prior to −0.3 V vs RHE (reversible hydrogen electrode). On the other hand, it is anticipated that Pt—C was very active for HER. Indeed, the Pt—C catalyst exhibited a catalytic onset at

nearly zero overpotential with a quick catalytic current increase along cathodic potential scanning. It was pleasant to see that a catalytic current rapidly rose for Ni—P when the potential was scanned more negative than −50 mV vs RHE (FIG. 15(a), inset). Vibrant H<sub>2</sub> bubble growth and release from the Ni—P film surface were observed upon further cathodic sweep. An overpotential of merely −93 mV was required for Ni—P to achieve a current density of 10 mA/cm<sup>2</sup>, which compares favorably to many other reported HER catalysts under strongly alkaline conditions. A detailed comparison is listed in Table 4:

TABLE 4

| Comparison of selected nonprecious HER electrocatalysts in alkaline media |             |                                |           |                                              |                                                  |
|---------------------------------------------------------------------------|-------------|--------------------------------|-----------|----------------------------------------------|--------------------------------------------------|
| Catalysts                                                                 | Electrolyte | j<br>(mA<br>cm <sup>−2</sup> ) | η<br>(mV) | Tafel<br>slope<br>(mV<br>dec <sup>−1</sup> ) | Reference                                        |
| Ni—P film                                                                 | 1M<br>KOH   | 10                             | 93        | 43                                           | This work                                        |
|                                                                           |             | 20                             | 110       |                                              |                                                  |
|                                                                           |             | 100                            | 160       |                                              |                                                  |
| Ni <sub>2</sub> P                                                         | 1M<br>KOH   | 20                             | 205       | N/A                                          | <i>J. Am. Chem. Soc.</i><br>2013, 135, 9267.     |
|                                                                           |             |                                |           |                                              |                                                  |
| Ni/Ni(OH) <sub>2</sub>                                                    | 0.1M<br>KOH | 10                             | >300      | 128                                          | <i>Angew. Chem. Int. Ed.</i><br>2012, 51, 12495. |
|                                                                           |             |                                |           |                                              |                                                  |
| Co—P film                                                                 | 1M<br>KOH   | 10                             | 94        | 42                                           | <i>Angew. Chem. Int. Ed.</i><br>2015, 54, 6251.  |
|                                                                           |             | 20                             | 115       |                                              |                                                  |
|                                                                           |             | 100                            | 158       |                                              |                                                  |
| CoP/CC                                                                    | 1M<br>KOH   | 10                             | 209       | 129                                          | <i>J. Am. Chem. Soc.</i><br>2014, 136, 7587.     |
|                                                                           |             | 100                            | >500      |                                              |                                                  |
| Co—S/FTO                                                                  | 1M<br>KOH   | 1                              | 480       | N/A                                          | <i>J. Am. Chem. Soc.</i><br>2013, 135, 17699.    |
|                                                                           |             |                                |           |                                              |                                                  |
| Co—<br>NRCNTs                                                             | 1M<br>KOH   | 10                             | 370       | N/A                                          | <i>Angew. Chem. Int. Ed.</i><br>2014, 53, 4372.  |
|                                                                           |             | 20                             | >450      |                                              |                                                  |
| MoB                                                                       | 0.1M<br>KOH | 10                             | 225       | 59                                           | <i>Angew. Chem. Int. Ed.</i><br>2012, 51, 12703. |
|                                                                           |             |                                |           |                                              |                                                  |
| MoS <sub>2+x</sub> /FTO                                                   | 1M<br>KOH   | 10                             | 310       | N/A                                          | <i>Angew. Chem. Int. Ed.</i><br>2015, 54, 667.   |
|                                                                           |             |                                |           |                                              |                                                  |
| Amorphous<br>MoS <sub>x</sub>                                             | 0.1M<br>KOH | 10                             | 540       | N/A                                          | <i>Chem. Sci.</i><br>2011, 2, 1262.              |
|                                                                           |             |                                |           |                                              |                                                  |
| FeP                                                                       | 1M<br>KOH   | 10                             | 218       | 146                                          | <i>ACS Catal.</i><br>2014, 4, 4065.              |
|                                                                           |             |                                |           |                                              |                                                  |
| NAs/CC                                                                    | KOH         |                                |           |                                              |                                                  |

**[0122]** Even more remarkably, the Ni—P film was able to produce a catalytic current density of 500 mA/cm<sup>2</sup> within an overpotential of −219 mV. The derived Tafel plot (FIG. 15(b)) clearly presents two kinetic regions. Linear fittings at the low and high overpotentials rendered Tafel slopes of 43 and 81 mV/dec, respectively. It is known that water dissociation might play a critical role under strongly alkaline conditions for H<sub>2</sub> evolution, especially when the proton supply is insufficient at high overpotentials. (See R. Subbaraman, D. Tripkovic, D. Strmcnik, K.-C. Chang, M. Uchimura, A. P. Paulikas, V. Stamenkovic, N. M. Markovic, *Science* 2011, 334, 1256-1260; and N. Danilovic, R. Subbaraman, D. Strmcnik, K.-C. Chang, A. P. Paulikas, V. R. Stamenkovic, N. M. Markovic, *Angew. Chem. Int. Ed.* 2012, 51, 12495-12498; *Angew. Chem.* 2012, 124, 12663-12666.) Therefore, the Tafel slope obtained at the low overpotential region (43 mV/dec) more likely represents the intrinsic HER catalytic activity of Ni—P. Such a small Tafel slope is among the smallest of reported HER catalysts in alkaline media (Table 4). Even though the onset potential of Ni—P is more negative than that of Pt—C, its Tafel slope is smaller than that of Pt—C (108 mV/dec), therefore it is anticipated that the catalytic current of Ni—P would surpass that of

Pt—C at high overpotentials. In contrast, the HER activity of NiO<sub>x</sub> is negligible under this condition, slowly showing catalytic current beyond −0.2 V vs RHE. Besides high efficiency for HER, the Ni—P film also exhibited excellent long-term stability. FIG. 15(c) shows the polarization curves of a Ni—P film prior to and post 1000 continuous cyclic voltammetric sweeps between 0 and −0.25 V vs RHE, whose perfect overlap confirmed the robustness of Ni—P for extended HER catalysis.

**[0123]** We next collected the SEM and XPS results of a post-HER Ni—P sample to determine possible morphology and composition change after a 2-h HER electrocatalysis at −110 mV vs RHE when stable catalytic current was achieved (FIG. 16). Its SEM image shown in FIG. 15(d) demonstrates that the post-HER film still maintained a uniform coverage on the copper foil and no apparent clusters or aggregates were observed. It is interesting to find that most of the original black holes disappeared, implying some catalyst rearrangement took place during HER electrocatalysis. Elemental mapping analysis further confirmed the even distribution of nickel and phosphorous in the post-HER film (data not shown). FIG. 13(c) also includes the high-resolution Ni 2p XPS spectrum of the post-HER film, exhibiting two peaks at 853.1 and 870.3 eV, corresponding to Ni 2p<sub>3/2</sub> and 2p<sub>1/2</sub> binding energies, respectively. Similarly, FIG. 13(d) displays its high-resolution P 2p spectrum showing a broad peak in 128-132 eV. In fact, these XPS features are very similar to those of the as-prepared Ni—P film, indicating the overall valence states of nickel and phosphorous did not evolve substantially during HER electrocatalysis. Moreover, the as-prepared and post-HER films exhibited similar capacitance, as shown in FIGS. 17(a)-17(c), suggesting their comparable electrochemically active surface area. Nevertheless, elemental analysis of the post-HER film resulted in nickel and phosphorous amounts of 1.06 and 0.21 mg/cm<sup>2</sup> with a Ni/P atomic ratio of 2.65. These values are smaller than the original mass of the as-prepared Ni—P, indicating some catalyst dissolution occurred during HER electrocatalysis.

**[0124]** The OER electrocatalytic performance of Ni—P was next assessed in the same electrolyte, 1.0 M KOH. FIG. 18(a) compares the polarization curves of Ni—P, commercially available IrO<sub>2</sub>, electrodeposited NiO<sub>x</sub>, and a blank copper foil. As expected, the blank copper foil is not an active OER catalyst, producing negligible anodic current before 1.7 V vs RHE. In contrast, the OER catalytic current of the Ni—P film increased dramatically beyond 1.50 V vs RHE (FIG. 18(a), inset), even comparable to the onset of IrO<sub>2</sub>. The Ni—P film was able to produce catalytic current densities of 10, 100, and 500 mA/cm<sup>2</sup> at η=344, 399, and 460 mV, respectively, lower than those of IrO<sub>2</sub> and many other reported OER catalysts, as shown in Table 5:

TABLE 5

| Comparison of selected nonprecious OER electrocatalysts in alkaline media. |             |                                           |                                              |           |
|----------------------------------------------------------------------------|-------------|-------------------------------------------|----------------------------------------------|-----------|
| Catalysts                                                                  | Electrolyte | η<br>(mV) at<br>10 mA<br>cm <sup>-2</sup> | Tafel<br>slope<br>(mV<br>dec <sup>-1</sup> ) | Reference |
| Ni—P film                                                                  | 1.0M<br>KOH | 344                                       | 49                                           | This work |

TABLE 5-continued

| Comparison of selected nonprecious OER electrocatalysts in alkaline media. |              |                                           |                                              |                                                 |
|----------------------------------------------------------------------------|--------------|-------------------------------------------|----------------------------------------------|-------------------------------------------------|
| Catalysts                                                                  | Electrolyte  | η<br>(mV) at<br>10 mA<br>cm <sup>-2</sup> | Tafel<br>slope<br>(mV<br>dec <sup>-1</sup> ) | Reference                                       |
| Ni <sub>2</sub> P nanowires                                                | 1.0M<br>KOH  | 400                                       | 60                                           | <i>Chem. Commun.</i><br>2015, 51, 11626.        |
| Ni <sub>2</sub> P                                                          | 1.0M<br>KOH  | 290-330                                   | 47-59                                        | <i>Energy Environ. Sci.</i> ,<br>2015, 8, 2347. |
| Co—P film                                                                  | 1.0M<br>KOH  | 345                                       | 47                                           | <i>Angew. Chem. Int. Ed.</i><br>2015, 54, 6251. |
| NiCo LDH                                                                   | 1.0M<br>KOH  | 367                                       | 40                                           | <i>Nano Lett.</i><br>2015, 15, 1421.            |
| Cu—N—C/<br>graphene                                                        | 0.1M<br>KOH  | >770                                      | N/A                                          | <i>Nat. Commun.</i><br>2014, 5, 5285.           |
| CoCo LDH                                                                   | 1.0M<br>KOH  | 393                                       | 59                                           | <i>Nat. Commun.</i><br>2014, 5, 4477.           |
| Co <sub>3</sub> O <sub>4</sub> /rm-GO                                      | 1.0M<br>KOH  | 310                                       | 67                                           | <i>Nat. Mater.</i><br>2011, 10, 780.            |
| MnO <sub>x</sub> /Au                                                       | 0.1M<br>KOH  | >480                                      | N/A                                          | <i>J. Am. Chem. Soc.</i><br>2014, 136, 4920.    |
| Ca <sub>2</sub> Mn <sub>2</sub> O <sub>5</sub> /C                          | 0.1M<br>KOH  | >470                                      | 149                                          | <i>J. Am. Chem. Soc.</i><br>2014, 136, 14646.   |
| Co <sub>x</sub> O <sub>y</sub> /NC                                         | 0.1M<br>KOH  | 430                                       | N/A                                          | <i>Angew. Chem. Int. Ed.</i><br>2014, 53, 8508. |
| De-LiCoO <sub>2</sub>                                                      | 0.1M<br>KOH  | >400                                      | 50                                           | <i>Nat. Commun.</i><br>2014, 5, 4345.           |
| CoMn LDH                                                                   | 1.0M<br>KOH  | 324                                       | 43                                           | <i>J. Am. Chem. Soc.</i><br>2014, 136, 16481.   |
| NiFeOx film                                                                | 1.0M<br>NaOH | >350                                      | N/A                                          | <i>J. Am. Chem. Soc.</i><br>2013, 135, 16977.   |
| CoO/NG                                                                     | 1.0M<br>KOH  | 340                                       | 71                                           | <i>Energy Environ. Sci.</i><br>2014, 7, 609.    |
| CoO <sub>x</sub> film                                                      | 1.0M<br>KOH  | 403                                       | 42                                           | <i>J. Am. Chem. Soc.</i><br>2012, 134, 17253.   |
| α-MnO <sub>2</sub> —SF                                                     | 0.1M<br>KOH  | 490                                       | 77.5                                         | <i>J. Am. Chem. Soc.</i><br>2014, 136, 11452.   |
| MnO <sub>x</sub> film                                                      | 1.0M<br>KOH  | 563                                       | 49                                           | <i>J. Am. Chem. Soc.</i><br>2012, 134, 17253.   |
| NiFeO <sub>x</sub> film                                                    | 1.0M<br>NaOH | >350                                      | N/A                                          | <i>J. Am. Chem. Soc.</i><br>2013, 135, 16977.   |
| Fe—Ni oxides                                                               | 1.0M<br>KOH  | >375                                      | 51                                           | <i>ACS Catal.</i><br>2012, 2, 1793.             |
| Zn <sub>x</sub> Co <sub>3-x</sub> O <sub>4</sub><br>nanowire               | 1.0M<br>KOH  | 330                                       | 51                                           | <i>Chem. Mater.</i><br>2014, 26, 1889.          |
| Ni <sub>x</sub> Co <sub>3-x</sub> O <sub>4</sub><br>nanowire               | 1.0M<br>KOH  | ~370                                      | 59-64                                        | <i>Adv. Mater.</i><br>2010, 22, 1926.           |

**[0125]** The quick surpass of Ni—P over IrO<sub>2</sub> in OER activity was well rationalized by their different Tafel slopes. As shown in FIG. 18(b), the linear fitting of their corresponding Tafel plots resulted in Tafel slopes of 49 mV/dec for Ni—P and 55 mV/dec for IrO<sub>2</sub>, indicating a more favorable OER kinetic rate of the former. Although NiO<sub>x</sub> was reported as a decent OER catalyst, its catalytic current did not take off until 1.6 V vs RHE and its Tafel slope was 65 mV/dec, inferior to those of Ni—P and IrO<sub>2</sub>. Besides great OER activity, our Ni—P film also featured excellent stability, as revealed by the overlap of its polarization curves before and after 1000 continuous cyclic voltammetric sweeps within the potential ranges of 1.50-1.65 V (FIG. 18(c)) and 1.0-1.7 V (FIG. 19) vs RHE. A redox feature of Ni<sup>III/II</sup> was observed around 1.3-1.4 V vs RHE in the latter, consistent with those reported nickel-based OER electrocatalysts. (See, L. D. Burke, T. A. M. Twomey, *J. Electroanal. Chem.* 1984, 162, 101-119; and M. Wehrens-Dijksma, P. H. L. Notten, *Electrochim. Acta* 2006, 51, 3609-3621.)

**[0126]** The SEM image of a Ni—P film after a 2-h OER electrolysis at η=350 mV in 1.0 M KOH is shown in FIG. 18(d). No apparent aggregates or particles were observed;

instead it still maintained an overall morphology analogous to those of the parent and post-HER Ni—P films. Despite no significant morphology change during OER, elemental analysis of the post-OER film demonstrates that a large amount of oxygen species were involved at least on the surface of the film (data not shown); while nickel and phosphorous atoms were still evenly distributed over the entire film. It is well anticipated that nickel and phosphorous would be oxidized under anodic conditions of OER. Indeed, the high-resolution Ni 2p XPS spectrum of the post-OER Ni—P film clearly presents the rise of a shoulder peak at ~856.5 eV (FIG. 13(c)), which can be attributed to nickel oxides/hydroxides. However, the dominant peaks are still located at 852.9 and 870.1 eV, close to those of the as-prepared and post-HER films. Similarly, a peak at 133.8 eV ascribed to oxidized phosphorous species (e.g., phosphate) is observed in the high-resolution P 2p XPS spectrum (FIG. 13(d)). Nevertheless, another P 2p peak at a lower binding energy region of 129-131 eV is still present. In addition, Raman spectra of the three Ni—P samples, as-prepared, post-HER, and post-OER, were collected and compared in FIG. 20. The Raman spectra of the as-prepared and post-HER samples are quite similar to each other, implying no substantial change in composition of the Ni—P film prior to and post HER. However, a prominent absorption peak was observed at 500-600  $\text{cm}^{-1}$  for the post-OER Ni—P film, indicating the formation of oxidized nickel species (e.g., nickel oxides and/or oxyhydroxides) on the catalyst surface. Fourier transform infrared spectroscopy (FTIR) of the post-OER electrolyte solution did not show apparent oxidized phosphorous species (e.g., phosphate), implying a very small amount of oxidized phosphorous would be dissolved in the electrolyte solution (FIG. 21).

[0127] Given the aforementioned results, we concluded that the Ni—P film was partially oxidized to nickel oxides/hydroxides during OER (most likely on the film surface), while the bulk composition of the post-OER film still retained as the original Ni—P. It should be noted that core-shell structure has been reported for  $\text{Ni}_2\text{P}$  nanowires as OER electrocatalysts, wherein the shell was mainly composed of nickel oxides/hydroxides while the core remained as  $\text{Ni}_2\text{P}$ . Elemental analysis of the post-OER film resulted in the remaining amounts of nickel and phosphorous as 1.24 and 0.29  $\text{mg}/\text{cm}^2$  with a Ni/P atomic ratio of 2.25. It is interesting to note that the control sample  $\text{NiO}_x$  which might also possess a metallic nickel core and a nickel oxide shell was unable to compete with our Ni—P in terms of both HER and OER activities, which undoubtedly prove the beneficial role that phosphorous plays in water splitting electrocatalysis.

[0128] Since the polarization-derived Tafel slopes aforementioned might overlook the impact of electron transport in the catalyst material on HER and OER performance, we further carried out detailed electrochemical impedance spectroscopy (EIS) studies to probe the intrinsic kinetics of our Ni—P films. The EIS data for both HER and OER electrocatalysis can be simulated by a semi-empirical electrical equivalent circuit model shown in FIG. 22, (See J. Kibsgaard, T. F. Jaramillo, F. Besenbacher, *Nat. Chem.* 2014, 6, 248-253.) whereas  $R_i$  and  $R_p$  represent the uncompensated solution resistance and kinetics of interfacial charge transfer, respectively.  $C_{dl}$  models the double layer capacitance.  $C_s$  and  $R_s$  in a parallel circuit simulate the relaxation of charges associated with adsorbed intermediates on catalyst surface.

The Nyquist plots of Ni—P for HER at overpotentials of -40 to -130 mV are displayed in FIG. 23(a), together with solid fitting curves. The corresponding Bode plots are shown in FIG. 24. The EIS-derived Tafel plot of  $\log R_p$  vs overpotential ( $\eta$ ) is included as an inset in FIG. 23(a). Analogous to the pattern of polarization-derived Tafel plot (FIG. 15(b)), two kinetic regions were observed, resulting in Tafel slopes of 33 and 98 mV/dec at low and high overpotentials, respectively. This is again consistent with insufficient proton supply when HER rate is very fast at high overpotentials. For OER electrocatalysis, the EIS data were collected at overpotentials of 270 to 360 mV and the Nyquist and Bode plots are displayed in FIGS. 23(b) and 25, respectively. The OER EIS results were also simulated by the same equivalent electrical circuit successfully and the solid fitting curves are included in FIG. 23(b) as well. FIG. 23(b) inset shows the EIS-derived Tafel plot of OER catalyzed by our Ni—P film, rendering a slope of 52 mV/dec, which is in a good agreement with the value resulting from the polarization-derived Tafel slope, 49 mV/dec (FIG. 18(b)).

[0129] The OER mechanism of the transformed Ni—P film was further studied by an investigation conducted in KOH of various concentrations. The polarization curves were collected in 1.0-5.0 M KOH (FIG. 26). The derived Tafel plots in FIG. 27(a) are nearly parallel to each other, indicating no kinetic change as the KOH concentration increased from 1.0 to 5.0 M. When plotting the potential requirements at current densities of 5 and 10  $\text{mA}/\text{cm}^2$  versus the logarithm of the hydroxide activity ( $[\text{OH}]_a$ ), two linear plots were obtained in FIG. 27(b). Fitting of these two plots led to slopes of 51.92 (for 5  $\text{mA}/\text{cm}^2$ ) and 51.88 (for 10  $\text{mA}/\text{cm}^2$ ) mV/dec, respectively. These slopes match the polarization-derived (49 mV/dec, FIG. 18(b)) and resistance-derived (52 mV/dec, FIG. 23(b)) Tafel slopes very well. According to Equation 1:

$$\left( \frac{\partial E}{\partial \log[\text{OH}]_a} \right) = \left( \frac{\partial \log}{\partial \log[\text{OH}]_a} \right) \left( \frac{\partial E}{\partial \log i} \right)_{\log[\text{OH}]_a} \quad \text{Equation 1}$$

the close match of

$$\frac{\partial E}{\partial \log[\text{OH}]_a} \quad \text{and} \quad \frac{\partial E}{\partial \log i}$$

results in the unity of

$$\frac{\partial \log i}{\partial \log[\text{OH}]_a}$$

(See Y. Surendranath, M. W. Kanan, D. G. Nocera, *J. Am. Chem. Soc.* 2010, 132, 16501-16509.) In other words, the OER reaction rate catalyzed by the Ni—P film is first order in the activity of hydroxide anion; therefore the limiting step is likely one hydroxide transfer, similar to the reported mechanism of “CoPi”. Id.

[0130] From the above results, it is natural to anticipate that the Ni—P film can be employed as a bifunctional electrocatalyst for overall water splitting. Indeed, when the as-prepared Ni—P films were used as electrocatalysts for

both anode and cathode (a Ni—P/Ni—P catalyst couple), a catalytic current was observed when the applied potential was larger than 1.55V (FIG. 28). The rapid catalytic current density rapidly exceeded 10 mA/cm<sup>2</sup> at 1.67 V. In addition, the Ni—P/Ni—P catalyst couple also maintained excellent stability, as revealed by the nearly overlap of the polarization curves before and after 1000 continuous potential cycles between 1.5 and 1.65 V (FIG. 28). Chronopotentiometry with a catalytic current of 10 mA/cm<sup>2</sup> was conducted for 24 h (FIGS. 29(a) and 29(b)), showing fairly stable performance of the Ni—P/Ni—P catalyst couple.

[0131] In summary, potentiodynamically deposited Ni—P films have been demonstrated to act as competent and bifunctional electrocatalysts for overall water splitting. The Ni—P film is unique because of the following reasons: (i) it is prepared via facile electrodeposition with low-cost reagents under an ambient condition and can be directly employed as an electrocatalyst for both HER and OER without any post treatment; (ii) the catalytic activity of the Ni—P film can rival the state-of-the-art catalysts (i.e., Pt and IrO<sub>2</sub>), requiring an  $\eta$ =−93 mV for HER and  $\eta$ =344 mV for OER to reach a current density of 10 mA/cm<sup>2</sup> with corresponding small Tafel slopes of 43 and 49 mV/dec, respectively; (iii) it can be utilized as catalysts for both anode and cathode of overall water splitting catalysis under strongly alkaline condition with superior efficiency and strong robustness. Various characterization and analytical techniques were applied to study the morphology and composition of the Ni—P film prior to and post electrocatalysis. It was concluded that the major component of the film is metallic nickel and nickel phosphide for the as-prepared and post-HER samples, whereas it was partially oxidized to nickel oxides/hydroxides/phosphates on the surface during OER. Kinetic analysis of its OER catalysis implied the limiting step is the transfer of one hydroxide group. Different from many reported hybrid systems, no conductive supports of high surface area, such as graphenes, carbon nanotubes, and nickel foams, were involved in the current system. The introduction of catalyst supports of high conductivity and large surface area will undoubtedly further boost the catalytic performance of the Ni—P film, which is under our current pursuit.

[0132] In the following part of the present specification, numbered examples are listed which are directed to and which define advantageous embodiments. Said examples and embodiments belong to the present disclosure and description. The embodiments, examples, and features as listed, can separately or in groups, be combined in any manner to form embodiments belonging to the present disclosure.

#### Numbered Examples

[0133] 1. A catalyst, comprising a conductive substrate coated with a metal-phosphorus-derived film, wherein the metal is selected from the group consisting of Manganese, Iron, Cobalt, Nickel, and Copper.

[0134] 2. The catalyst of example 1, wherein the conductive substrate comprises a material selected from the group consisting of copper, titanium, glassy carbon, fluorine-doped tin oxide, indium-doped tin oxide, tin, nickel, and stainless steel.

[0135] 3. The catalyst of examples 1-2, wherein the metal-phosphorus-derived film is electrodeposited.

[0136] 4. The catalyst of examples 1-3, wherein the metal-phosphorus-derived film comprises a cobalt-phosphorous-derived film.

[0137] 5. The catalyst of examples 1-4, wherein the conductive substrate comprises a material selected from the group consisting of copper foil, nickel, and stainless steel.

[0138] 6. The catalyst of examples 1-5, wherein the metal-phosphorus-derived film has a phosphorus concentration of greater than 0 to about 50%.

[0139] 7. The catalyst of examples 1-5, wherein the metal-phosphorus-derived film has a phosphorus concentration of from about 5% to about 50%.

[0140] 8. The catalyst of examples 1-5, wherein the metal-phosphorus-derived film has a phosphorus concentration of from about 5% to about 20%.

[0141] 9. The catalyst of examples 1-5, wherein the metal-phosphorus-derived film has a phosphorus concentration of about 10%.

[0142] 10. A method of producing hydrogen gas or oxygen gas, the method comprising:

[0143] providing a electrolysis solution, the electrolysis solution comprising water and an electrolyte;

[0144] inserting the catalyst of claim 1 into the electrolysis solution;

[0145] running an electric current through the catalyst.

[0146] 11. The method of example 10, further comprising identifying and quantifying the hydrogen gas or oxygen gas.

[0147] 12. The method of examples 10-11, further comprising collecting the hydrogen gas.

[0148] 13. The method of examples 10-12, further comprising collecting the oxygen gas.

[0149] 14. The method of examples 10-13, wherein the catalyst comprises a cobalt-phosphorous-derived film on a conductive substrate.

[0150] 15. The method of examples 10-14, wherein the conductive substrate comprises copper foil.

[0151] 16. The method of examples 10-15, wherein the electrolysis solution comprises an alkaline electrolyte.

[0152] 17. The method of examples 10-16, wherein the electrolysis solutions is selected from the group consisting of KOH and NaOH.

[0153] 18. A method of producing a catalyst, the method comprising:

[0154] providing a working electrode and a counter electrode, the working electrode and counter electrode each comprising a conductive substrate;

[0155] electrodepositing on the working electrode a metal-phosphorus-derived film, wherein the metal is selected from the group consisting of Manganese, Iron, Cobalt, Nickel, and Copper.

[0156] 19. The method of example 18, wherein electrodepositing comprises:

[0157] submersing the working electrode and the counter electrode in a deposition solution comprising a metal source that comprises Manganese, Iron, Cobalt, Nickel, or Copper and a phosphorus source, and

[0158] cycling a current through the working electrode and counter electrode.

[0159] 20. The method of examples 18-19, wherein:

[0160] the metal source comprises CoSO<sub>4</sub> and

[0161] the phosphorus source comprises NaH<sub>2</sub>PO<sub>2</sub>.

[0162] 21. The method of examples 18-20, wherein the current is cycled between a potential of −0.3 and −1.0 V vs Ag/AgCl.

[0163] It will be appreciated that various of the above-disclosed and other features and functions, or alternatives thereof, may be desirably combined into many other different systems or applications. Also, various presently unforeseen or unanticipated alternatives, modifications, variations or improvements therein may be subsequently made by those skilled in the art, and are also intended to be encompassed by the following claims.

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What is claimed is:

1. A catalyst, comprising a conductive substrate coated with a metal-phosphorus-derived film, wherein the metal is selected from the group consisting of Manganese, Iron, Cobalt, Nickel, and Copper.
2. The catalyst of claim 1, wherein the conductive substrate comprises a material selected from the group consisting of copper, titanium, glassy carbon, fluorine-doped tin oxide, indium-doped tin oxide, tin, nickel, and stainless steel.
3. The catalyst of claim 1, wherein the metal-phosphorus-derived film is electrodeposited.
4. The catalyst of claim 1, wherein the metal-phosphorus-derived film comprises a cobalt-phosphorous-derived film.
5. The catalyst of claim 1, wherein the conductive substrate comprises a material selected from the group consisting of copper foil, nickel, and stainless steel.
6. The catalyst of claim 1, wherein the metal-phosphorus-derived film has a phosphorus concentration of greater than 0 to about 50%.
7. The catalyst of claim 1, wherein the metal-phosphorus-derived film has a phosphorus concentration of from about 5% to about 50%.
8. The catalyst of claim 1, wherein the metal-phosphorus-derived film has a phosphorus concentration of from about 5% to about 20%.

9. The catalyst of claim 1, wherein the metal-phosphorus-derived film has a phosphorus concentration of about 10%.

10. A method of producing hydrogen gas or oxygen gas, the method comprising:

providing a electrolysis solution, the electrolysis solution comprising water and an electrolyte;

inserting the catalyst of claim 1 into the electrolysis solution;

running an electric current through the catalyst.

11. The method of claim 10, further comprising identifying and quantifying the hydrogen gas or oxygen gas.

12. The method of claim 10, further comprising collecting the hydrogen gas.

13. The method of claim 10, further comprising collecting the oxygen gas.

14. The method of claim 10, wherein the catalyst comprises a cobalt-phosphorous-derived film on a conductive substrate.

15. The method of claim 10, wherein the conductive substrate comprises copper foil.

16. The method of claim 10, wherein the electrolysis solution comprises an alkaline electrolyte.

17. The method of claim 10, wherein the electrolysis solutions is selected from the group consisting of KOH and NaOH.

18. A method of producing a catalyst, the method comprising:

providing a working electrode and a counter electrode, the working electrode and counter electrode each comprising a conductive substrate;

electrodepositing on the working electrode a metal-phosphorus-derived film, wherein the metal is selected from the group consisting of Manganese, Iron, Cobalt, Nickel, and Copper.

19. The method of claim 18, wherein electrodeposition comprises:

submersing the working electrode and the counter electrode in a deposition solution comprising a metal source that comprises Manganese, Iron, Cobalt, Nickel, or Copper and a phosphorus source, and

cycling a current through the working electrode and counter electrode.

20. The method of claim 19, wherein:  
the metal source comprises  $\text{CoSO}_4$  and  
the phosphorus source comprises  $\text{NaH}_2\text{PO}_2$ .

\* \* \* \* \*