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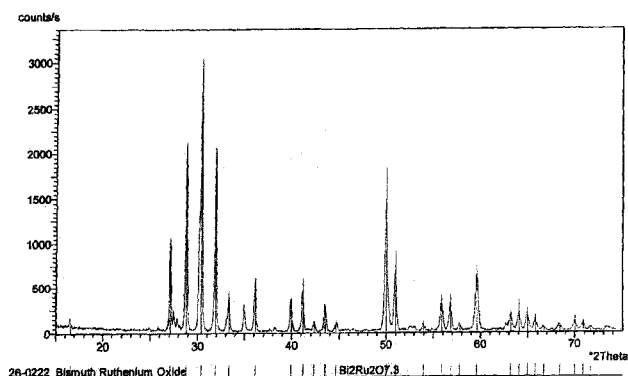


Fig. 1

(57) Abstract: Novel bismuth based mixed metal oxide materials with pyrochlore structure are disclosed as anodes for electrolytic generation of ozone and perchlorate salts. These materials have high electrical conductivity and excellent stability in acidic electrolytes. These materials are more environmentally friendly than lead dioxide and less expensive than platinum.

## BISMUTH METAL OXIDE PYROCHLORES AS ELECTRODE MATERIALS FOR ELECTROLYTIC OZONE AND PERCHLORATE GENERATION

### CROSS-REFERENCE TO RELATED APPLICATION

**[0001]** This application claims the benefit of U.S. Provisional Application No. 61/218,554, filed June 19, 2009, entitled “Bismuth Metal Oxide Pyrochlores as Electrode Materials for Electrolytic Ozone and Perchlorate Generation,” the entire disclosure of which is hereby incorporated by reference.

### BACKGROUND OF THE INVENTION

**[0002]** The present invention pertains to Bi-based mixed metal oxide anode materials with pyrochlore structure which are shown to be active as anode electrocatalyst materials for generating ozone and perchlorate. The invention further relates to an ozone or perchlorate generator for producing ozone through the electrolytic decomposition of water or oxidation of chloride salts.

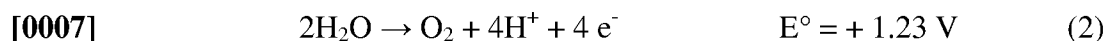
**[0003]** Ozonized water can be effectively used in the Medical, Food, Beverage and Agricultural (MFBA) industries as an antibacterial cleaning agent, as an oxidant and as pesticide. Ozone usage has recently been extended over to the semi-conductor industry for cleaning electronic components. C. Gottschalk, A. Saupe, and J. A. Libra, “Ozonation of water and waste water: a practical guide to understanding ozone and its application,” Wiley-VCH, New York, (2000). Ozone is primarily produced from air by either electrical discharge or by exposure to UV radiation. However, since air contains 80% of nitrogen, oxidation of nitrogen to nitrogen oxides also occurs. When the ozone thus produced is dissolved in water to produce ozonized water, the nitrogen oxides also dissolve thereby imparting acidity to the water. Also, due to low partial pressure of ozone in the gas phase and limited solubility of ozone in water, the concentration of ozone in water will be low using this method.

**[0004]** Alternatively ozone can be generated from water by electrolysis as shown in the anode reaction set forth in Equation (1) below and described in W. G. Fischer, “Electrolytical ozone production for super-pure water disinfection,” *Pharma International*, 2, 1997.

**[0005]** 
$$3\text{H}_2\text{O} \rightarrow \text{O}_3 + 6\text{H}^+ + 6\text{e}^- \quad \text{E}^\circ = + 1.49 \text{ V} \quad (1)$$

**[0006]** Ozone thus produced is present in water in high concentrations, and no issues with acidity or solubility are present. A disadvantage of this process is the high voltage of the

reaction, which increases the power consumption. Also, the efficiency of the process is low because oxygen evolution competes with ozone production as set forth in Equation (2) below. Hydrogen evolution (Equation 3) is the cathodic reaction.



[0008] Hydrogen evolution occurs at the cathode according to Equation (3) below.



[0010] Usage of lead dioxide ( $\text{PbO}_2$ ) as an anode material for producing ozone has been described in the literature. P. C. Foller and C. W. Tobias, "The anodic evolution of Ozone," *J. Electrochem. Soc.*, 129 (3), 506 (1982). Commercial electrolytic ozonators based on  $\text{PbO}_2$  anodes are available. S. Stucki, et al., "In Situ production of Ozone in water using a Membrel electrolyzer", *J. Electrochem. Soc.*, 132 (2), 367 (1985).

[0011] In a typical process using  $\text{PbO}_2$ ,  $\text{O}_3$  is evolved into a stream of water from the back of a porous  $\text{PbO}_2$  anode in contact with a Nafion membrane electrolyte. However lead dioxide anode is not completely stable at high current densities ( $>1 \text{ A/cm}^2$ ) required for ozone generation.  $\text{PbO}_2$  decomposes and enters the ozonized water as plumbate *ions* contaminating the water and preventing the water from being used directly for many cleaning and MFBA applications. In order to produce lead-free ozonized water, the ozone gas must first be retrieved from ozonized water containing lead and then re-dissolved in fresh water before the ozone decomposes to oxygen. These additional steps make the process impractical. Hence, it is preferable that lead-free ozonized water be produced to be used directly for the cleaning or MFBA application.

[0012] Platinum is one of the few other candidate anode materials for electrolytic generation of ozone that has been considered for usage in commercial ozonators. See, U.S. Pat. No. 4,541,989. Use of Pt as the anode instead of a detrimental heavy metal, such as lead, allows production of ozonized water for MFBA and semi-conductor industry applications. However, Pt is not presently used in commercial ozonators because of its high cost and poor long term performance, i.e., ozone generation efficiency drops quickly compared to lead dioxide. On prolonged ozone generation, the Pt anode loses its activity due to: (1) degradation of Pt anode surface due to formation of either catalytically inactive or non-conductive surface coating and (2) degradation of the interface between Pt anode and the Nafion electrolyte. Even Pt is known to dissolve at high anodic current densities and enter the electrolyte.

[0013] Boron-doped diamond (BDD) with boron/carbon ratios of 100, 1000 and 5000 ppm are also potential anode materials for electrolytic ozone generation. See, U.S. Pat. No.

6,235,186. The overpotential for oxygen evolution was found to be > 2.0 V, which is significantly larger, compared to PbO<sub>2</sub> anodes. Increasing the Boron doping lowers the oxygen evolution overpotential. However, current efficiencies for ozone generation were approximately one third of those obtained with PbO<sub>2</sub> electrodes. During final stages of the electrolysis, a sharp increase in voltage is observed for all the three doped materials but the higher B-doped material lasted longer. The failure is attributed to the spalling of the film from the substrate caused by the stress that was created during the production process of the films at high temperatures. N. Katsuki et al., "Water electrolysis using Boron-doped Diamond thin film electrodes", *J. Electrochem. Soc.*, 145 (7), 2358 (1998).

**[0014]** From the foregoing, PbO<sub>2</sub> materials used as anodes in current ozonators cannot be used for the MFBA and semi-conductor cleaning applications. Pt and boron-doped diamond (BDD) can potentially be used but they do not provide long cycle life. It would be an advancement in the art to provide an alternative, lead-free electrode material suitable for use in the electrolytic generation of ozone.

**[0015]** While the foregoing discussion has focused on the production of ozone, the electrochemical synthesis of perchlorate salts from chloride or chlorate salts typically uses PbO<sub>2</sub>, Pt or other electrodes with high oxygen overpotentials. These are the same types of electrodes used to generate ozone. Chlorates can be oxidized in an electrochemical cell to yield perchlorates. One common starting material is sodium chlorate, which may be oxidized at the anode according to the following reaction:



**[0017]** Sodium chlorate may be produced from sodium chloride according to the following reaction:



**[0019]** The energy efficiency of these reactors is as low as 20-40%. D. Pletcher and F.C. Walsh (1990), *Industrial Electrochemistry*, Chapman and Hill, New York. It would be an advancement in the art to provide anode materials for the preparation of perchlorate salts which are lead-free and which may provide higher current efficiency and longer life.

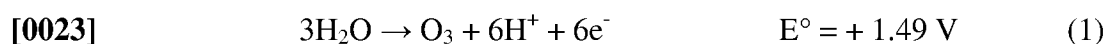
#### BRIEF SUMMARY OF THE INVENTION

**[0020]** The present invention provides bismuth mixed metal oxide pyrochlore materials suitable as high current density electrodes for electrolytic ozone and perchlorate generation. The bismuth mixed metal oxide pyrochlore materials disclosed herein provide safe and

effective replacement where lead dioxide electrodes are currently used for ozone and perchlorate generation.

**[0021]** The high current density electrodes used in connection with the invention comprise bismuth mixed metal oxide pyrochlore materials having the general formula  $A_2B_2O_{7-x}$ , where A is Bi and B is Ru, Ir, Rh, Sn, Ti, or Pt and  $0 \leq x \leq 1$ . In one non-limiting embodiment within the scope of the invention, B is Ru and the pyrochlore material has the general formula  $Bi_2Ru_2O_{7-x}$ , where  $0 \leq x \leq 1$ . In another non-limiting embodiment, the electrode may be fabricated of a composite of the bismuth mixed metal oxide pyrochlore material and one or more noble metals selected from Pt, Ag, Au, Ru, Re, or Pd. Electrolytic cells and electrolytic methods within the scope of the present invention have an anode which comprises a bismuth mixed metal oxide pyrochlore material as described above. The cathode may optionally comprise a bismuth mixed metal oxide pyrochlore material. The cathode material may be the same or different material as the anode.

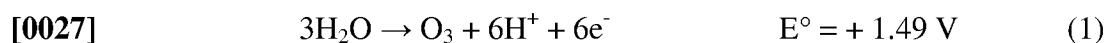
**[0022]** The invention includes an electrolytic method of generating ozone using an electrolytic cell having an anode comprising a bismuth mixed metal oxide pyrochlore material as described above. The electrolytic cell anode is operated at a current density sufficient to generate ozone. In one embodiment, the ozone is generated according to the reaction:



**[0024]** This reaction requires high current density, typically greater than  $1 \text{ A/cm}^2$ . In some non-limiting embodiments, the current density is greater than  $1.2 \text{ A/cm}^2$ . In other non-limiting embodiments, the current density greater than about  $1.4 \text{ A/cm}^2$ . In yet another non-limiting embodiment, the electrolytic cell anode is operated at a current density of approximately  $1.5 \text{ A/cm}^2$ . It will be appreciated by those of skill in the art that other reactions may be used to produce ozone under certain conditions. One such non-limiting reaction may include:



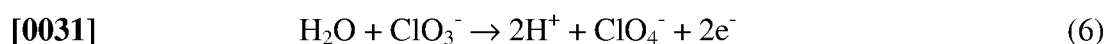
**[0026]** The invention includes an electrolytic cell for generating ozone. The electrolytic cell has an anode comprising a bismuth mixed metal oxide pyrochlore material as described above. The electrolytic cell further includes a cathode, electrolyzable water in contact with the anode and the cathode, and a source of electric potential and current electrically coupled to the anode and the cathode to produce an operating current density sufficient to generate ozone. In one embodiment, the ozone is generated at the anode according to the reaction.



[0028] The electrolytic cell may be operated at the current densities described above. The anode and cathode may be configured as described above. It will be appreciated by those of skill in the art that other reactions may be used to produce ozone under certain conditions. One such non-limiting reaction may include:

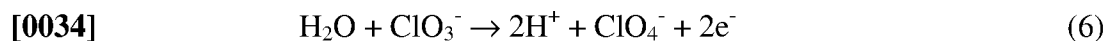


[0030] The invention includes an electrolytic method of generating a perchlorate salt using an electrolytic cell having an anode comprising a bismuth mixed metal oxide pyrochlore material as described above. The electrolytic cell anode is operated at a current density sufficient to oxidize a chlorate salt in aqueous solution to form a perchlorate salt in aqueous solution according to the reaction:



[0032] In one non-limiting embodiment, the chlorate and perchlorate salt is a sodium chlorate and perchlorate salt. This reaction requires high current density, typically greater than about 0.5 A/cm<sup>2</sup>, preferably greater than about 1.0 A/cm<sup>2</sup>, and more preferably in the range from 0.5 A/cm<sup>2</sup> and 1.3 A/cm<sup>2</sup>.

[0033] The invention includes an electrolytic cell for generating a perchlorate salt. The electrolytic cell has an anode comprising a bismuth mixed metal oxide pyrochlore material as described above. The electrolytic cell further includes a cathode, a chlorate salt in aqueous solution in contact with the anode, and a source of electric potential and current electrically coupled to the anode and the cathode to produce an operating current density sufficient to oxidize a chlorate salt in aqueous solution to form a perchlorate salt in aqueous solution at the anode according to the reaction.



[0035] The electrolytic cell may be operated at the current densities described above. The anode and cathode may be configured as described above.

[0036] While the foregoing discussion has focused on the use of a bismuth mixed metal oxide pyrochlore material as an anode material for the electrolytic preparation of ozone or perchlorate salt, it will be appreciated by those of skill in the art that the disclosed bismuth mixed metal oxide pyrochlore materials may be used in other electrochemical applications where high current density electrodes are needed.

[0037] These features and advantages of the present invention will become more fully apparent from the following description and appended claims, or may be learned by the practice of the invention as set forth hereinafter.

## BRIEF DESCRIPTION OF THE SEVERAL DRAWINGS

[0038] In order that the manner in which the above-recited and other features and advantages of the invention are obtained and will be readily understood, a more particular description of the invention briefly described above will be rendered by reference to specific embodiments thereof that are illustrated in the appended drawings. Understanding that the drawings depict only typical embodiments of the invention and are not therefore to be considered to be limiting of its scope, the invention will be described and explained with additional specificity and detail through the use of the accompanying drawings in which:

[0039] Figure 1 is an X-ray diffraction pattern of a synthesized bismuth ruthenium oxide;

[0040] Figure 2 shows a Rotating Ring Disk Electrode (RRDE) to study ozone generation;

[0041] Figure 3 is an X-ray diffraction pattern of sintered bismuth ruthenium oxide;

[0042] Figure 4 is a scanning electron micrograph (SEM) of a sintered bismuth ruthenium oxide disk;

[0043] Figure 5 is an energy dispersive X-ray spectroscopy (EDS) pattern of the bismuth ruthenium oxide sintered disk of Fig. 4;

[0044] Figure 6 is a cyclic voltammogram of the  $\text{Bi}_2\text{Ru}_2\text{O}_7$  disk in 5M phosphoric acid showing significant anodic current;

[0045] Figure 7 is a graph of  $\text{Bi}_2\text{Ru}_2\text{O}_7$  disk electrolysis with ozone collection on a Pt ring in 5M phosphoric acid at 10 mV/s in oxygen;

[0046] Figure 8 is a SEM image of the bismuth ruthenium oxide disk after electrolysis;

[0047] Figure 9 is an EDS of the bismuth ruthenium oxide disk after electrolysis;

[0048] Figure 10 is a schematic representation of an ozonator experimental setup;

[0049] Figure 11 is a graph showing detection of  $\text{O}_3$  (sparged from a corona discharge ozonator) using Au disk in 5M  $\text{H}_2\text{SO}_4$ ;

[0050] Figure 12 is a graph showing the operating performance parameters of voltage, temperature, and ozone current for an ozonator using a  $\text{Bi}_2\text{Ru}_2\text{O}_7$  coated Pt current collector; and

[0051] Figure 13 is a graph showing the operating performance parameters of voltage, temperature, and ozone current for an ozonator using a  $\text{Bi}_2\text{Ru}_2\text{O}_7$  coated Pt current collector.

## DETAILED DESCRIPTION OF THE INVENTION

[0052] Reference throughout this specification to “one embodiment,” “an embodiment,” or similar language means that a particular feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment of the present invention. Thus, appearances of the phrases “in one embodiment,” “in an embodiment,” and

similar language throughout this specification may, but do not necessarily, all refer to the same embodiment.

**[0053]** Furthermore, the described features, structures, or characteristics of the invention may be combined in any suitable manner in one or more embodiments. In the following description, numerous specific details are provided, such as examples of suitable bismuth mixed metal oxide pyrochlore materials, to provide a thorough understanding of embodiments of the invention. One having ordinary skill in the relevant art will recognize, however, that the invention may be practiced without one or more of the specific details, or with other methods, components, materials, and so forth. In other instances, well-known structures, materials, or operations are not shown or described in detail to avoid obscuring aspects of the invention.

**[0054]** Bismuth mixed metal oxide pyrochlore materials are disclosed herein as high current density electrodes for electrolytic ozone and perchlorate generation. The bismuth mixed metal oxide pyrochlore materials disclosed herein provide safe and effective lead-free electrode materials suitable for preparing ozonized water used in the medical, food, beverage and agricultural (MFBA) industries as an antibacterial cleaning agent, as an oxidant and as a pesticide. Such ozonized water may also be used in the semi-conductor industry for cleaning electronic components. The bismuth mixed metal oxide pyrochlore materials disclosed herein may also be used in an anode for the electrochemical preparation of perchlorate salts.

**[0055]** The high current density electrodes used in connection with the invention comprise bismuth mixed metal oxide pyrochlore materials having the general formula  $A_2B_2O_{7-x}$ , where A is Bi and B is Ru, Ir, Rh, Sn, Ti, or Pt and  $0 \leq x \leq 1$ . The electrode may be fabricated of a composite of the bismuth mixed metal oxide pyrochlore material and one or more noble metals selected from Pt, Ag, Au, Ru, Re, or Pd. Electrolytic cells and electrolytic methods within the scope of the present invention have an anode which comprises a bismuth mixed metal oxide pyrochlore material as described above. The cathode may optionally comprise a bismuth mixed metal oxide pyrochlore material. The cathode material may be the same or different material as the anode.

**[0056]** Bismuth ruthenium oxide ( $Bi_2Ru_2O_7$ ) is a known conducting material that may be used as an alternative to lead dioxide and platinum as anodes for ozone and perchlorate salt generation.  $Bi_2Ru_2O_7$  possesses the pyrochlore structure. It is known to exhibit stability in acidic as well as basic solutions under oxidizing conditions. J. M. Zen, R. Manoharan and J. B. Goodenough, *J. Appl. Electrochem.*, 22 140 (1992). Extensive oxygen and chlorine evolution capability, high initial electrocatalytic activity for oxygen reduction and



electrochemical oxidation of a number of organic compounds has been reported for this material. H. S. Horowitz, J. M. Longo and H. H. Horowitz, *J. Electrochem. Soc.*, 130, 1851 (1983); J. Praksah, A. K. Shukla and E. Yeager, *J. Power Sources*, 29, 413 (1990); N. M. Markovic and P. N. Ross, Jr. *J. Electrochem. Soc.*, 141 2590 (1994).

[0057] Jacobson et al., (U.S. Pat. No. 5,105,053) disclosed bismuth ruthenium oxide catalyst having the pyrochlore structure as an efficient catalyst for the conversion of hydrocarbons, and most preferably methane, to higher hydrocarbons and olefins.

[0058] U.S. Pat. No. 4,163,706 discloses synthesis and characterization of high surface area bismuth rich pyrochlore-type compounds containing ruthenium, iridium and mixtures thereof for application in electrochemical processes, such as electrocatalysis. U.S. Pat. No. 4,129,525 discloses lead-enriched and bismuth pyrochlore compounds with ruthenium and iridium to be useful in a catalytic or electrocatalytic environment. Similar disclosures are included in U.S. Pat. Nos. 4,203,871; 4,225,469; 4,434,031; and 4,440,670.

[0059] U.S. Pat. No. 4,146,458 discloses an electrochemical device which has an oxygen electrode containing a pyrochlore type material. Preferred pyrochlore materials have high lead content and the formula  $Pb_2[M_{2-x}Pb_x]O_{7-y}$ , where M is Ru or Ir and where  $0 \leq x \leq 1.2$  and  $0 \leq y \leq 1.0$ . Bismuth ruthenium oxide is within the scope of the broad disclosure.

[0060] Applicants are not aware of reported studies on the use or performance of this material as an anode for electrolytic ozone and perchlorate evolution.

[0061] To better explain the bismuth mixed metal oxide pyrochlore materials, several representative embodiments of suitable fabrication methods and electrolytic applications are described with reference to Figures 1-13. While the described bismuth mixed metal oxide pyrochlore materials may be used to make other perchlorate salts, for the sake of simplicity, the following examples discuss methods for using the electrode materials to produce ozone.

[0062] The following non-limiting examples are given to illustrate various embodiments within the scope of the present invention. This example is given by way of demonstration only, and it is understood that the following example is not comprehensive or exhaustive of the many types of embodiments of the present invention that can be prepared in accordance with the present invention.

[0063] EXAMPLE 1

[0064] Synthesis of  $Bi_2Ru_2O_7$ . Stoichiometric amounts of  $Bi_2O_3$  and  $RuO_2 \cdot xH_2O$  (the concentration of  $RuO_2$  and  $H_2O$  were determined by thermal gravimetric analysis (TGA) to be 76% and 24% respectively) were made into slurry by adding water and mixing with mortar and pestle. After mixing for 15 minutes, a consistent slurry was formed. The slurry

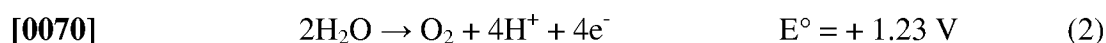
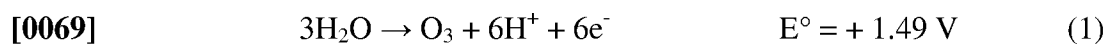
was then dried in a drying oven and again mixed with pestle before heating at 650 °C for 24 hours followed by 750 °C for 24 hours. X-ray diffraction (XRD) was performed at each stage to determine the phase purity of the product. The XRD results are shown in Figure 1. XRD data after the 750 °C step matched well with the Joint Committee on Powder Diffraction Standards (JCPDS) reference pattern with  $\text{Bi}_2\text{Ru}_2\text{O}_{7.3}$  except for 2 peaks. These peaks could not be attributed to either of the starting materials  $\text{Bi}_2\text{O}_3$  and  $\text{RuO}_2$ . Additional heating at 750 °C for another 24 hours did not change the intensity of the two peaks. Hence it was concluded that these peaks may be either due to some polymorph of starting material or a different (non pyrochlore) phase of bismuth and ruthenium. However, this second phase represent a relatively small proportion (< 10%) and isn't significant.

**[0065] EXAMPLE 2**

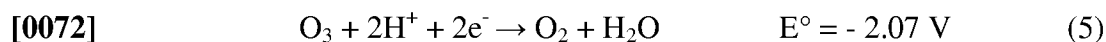
**[0066]** Rotating Ring Disk Electrode for Ozone analysis. A Rotating Ring Disk Electrode (RRDE) method was used to demonstrate that bismuth ruthenate can indeed function as an anode in electrolytic ozonator. A cross-sectional side view and bottom view of a typical RRDE device is shown in Figure 2. The theory behind the application of RRDE for in-situ generation/detection of ozone is briefly as follows. The RRDE 100 consists of a central disk electrode 102 surrounded by a concentric ring electrode 104 with a thin Teflon U-cup insulator 106 separating them. The potential or the current at each electrode can be controlled independently using a bipotentiostat (not-shown). A bipotentiostat controls the voltage and measures the current at two working electrodes immersed in an electrolyte, using only one reference electrode and one counter electrode. The RRDE shown in Figure 2 can be used to detect and measure  $\text{O}_3$  that is generated at the disk of RRDE. When the central disk electrode 102 is anodically polarized, ozone generated at the central disk electrode 102 can be quantitatively detected at the ring electrode 104 held at a potential where ozone is reduced ( $E^\circ = 2.07 \text{ V vs. NHE}$ ). Alternatively the ring electrode can be swept in the potential region where the ozone can be reduced. Thus, depending on the amount of ozone being generated at the disk electrode 102, the limiting ozone reduction current at the ring electrode 104 for each material could be determined. Hence, this method allows comparison of various anode materials for their ozone generation capacity.

**[0067]** The relevant electrode reactions which occur in the RRDE are set forth below:

**[0068]** Central disk electrode reactions:



**[0071]** Ring electrode reaction:



[0073] EXAMPLE 3

[0074] Preparation of the  $\text{Bi}_2\text{Ru}_2\text{O}_7$  RRDE disk. The synthesized  $\text{Bi}_2\text{Ru}_2\text{O}_7$  product from Example 1 was mixed with aqueous suspension of polyvinyl alcohol binder to coat the particles with the binder. The  $\text{Bi}_2\text{Ru}_2\text{O}_7$  material and binder were pressed into pellets and fired at 1100 °C in air for 24 hours. The XRD pattern for the sintered material is shown in Figure 3. The XRD pattern indicates that the crystal structure of the sintered material is quite different from the starting material. The identity of this material phase is not presently known. The final diameter of the pellets was ~ 0.6 mm. The pellets were further ground to the size and shape of the RRDE disk for use in the RRDE setup. The surface of the disk was also polished to further smooth the surface. Conductive silver paint was applied on the back side of the disk and cured at 700 °C. This was done to ensure good electrical contact between the metal spring of the RRDE and the mixed metal oxide disk. Scanning electron micrograph (SEM) and energy dispersive X-ray spectroscopy (EDS) analysis were performed on the disk. SEM data reported Figure 4 show that the surface of the disk has significant porosity that formed during the sintering process. EDS data reported in Figure 5 reveal no additional elements other than the expected Bi, Ru and O.

[0075] EXAMPLE 4

[0076] Cyclic voltammetry. Cyclic voltammetry (CV) of the disk prepared in Example 3 was performed in 5M  $\text{H}_3\text{PO}_4$  in an oxygen atmosphere. The CV data reported in Figure 6 shows that oxygen evolution starts at anodic polarization potentials of > 1.5 V, and that large currents are obtained at higher potentials as in the case of Pt and Pb disks. The material was also fairly active towards hydrogen evolution when polarized cathodically. Constant potential electrolysis at 4 V showed that  $\text{Bi}_2\text{Ru}_2\text{O}_7$  sustained a current density of 1.5 A/cm<sup>2</sup> for up to an hour without decay. EDS analysis on the residue retrieved by filtering the electrolyte showed no Bi or Ru peaks. Longer-term electrolysis experiments are required to generate more soluble species for chemical analysis.

[0077] EXAMPLE 5

[0078] Constant potential. Constant potential electrolysis experiments were performed with the  $\text{Bi}_2\text{Ru}_2\text{O}_7$  disk electrode prepared in Example 3. The disk electrode was kept at 4 V (the potential was predetermined such that the disk current was ~ 1.5 A/cm<sup>2</sup>) to produce ozone for subsequent collection at the ring. The ring potential was swept in the potential window for ozone reduction of 0.5 to 1.2 V. The CV of the ring during disk electrolysis is shown in Figure 7. There is significant ring current for ozone reduction when disk was being

electrolyzed indicating that ozone was being generated at the disk. The CV of the ring before and after electrolysis showed no such cathodic current due to ozone reduction. Since no cathodic current was observed on the ring after electrolysis, it appears that ozone generated during electrolysis was responsible for the current and not any soluble species formed due to decomposition of the  $\text{Bi}_2\text{Ru}_2\text{O}_7$  disk.

[0079] Some amount of physical disintegration of the disk was noticed on prolonged gas generation, recognizable by small amounts of solid material at the bottom of the cell. Scanning electron micrograph (SEM) images of the disk after electrolysis revealed that small portions of the electrode from the surface were lost as shown in Figure 8. EDS analysis revealed presence of Ag on the surface as shown in Figure 9. This unexpected result could be because of the porous nature of the sintered disk. The electrolyte may have penetrated the disk and attacked the silver that was applied on the back side. Based on these results, it appears that  $\text{Bi}_2\text{Ru}_2\text{O}_7$  disk is a good choice for ozone evolution. The RRDE experiments confirmed that bismuth ruthenium oxide ( $\text{Bi}_2\text{Ru}_2\text{O}_7$ ) may be successfully used as an anode material for the electrolytic generation of ozone.

[0080] Setup of Ozonator

[0081] Generation of ozone by electrolysis of water is well documented and a few variations of the experimental setup are known. The schematic of the experimental setup 200 adopted for the tests reported herein is shown in Figure 10. The setup used soft water generated by passing tap water through a commercial water softener. A soft water source 202 continuously fed soft water 204 to the electrolytic cell 206. The flow rate of the water 204 was varied as desired. A current of 30A ( $1.5\text{A}/\text{cm}^2$ ) was applied to the cell 206. Water with oxygen/ozone 208 exited the anode compartment and was separated in the gas-liquid separator 210. The feed water collected from the gas-liquid separator was discarded 212. The gaseous mixture 214 was then sparged into the Rotating Ring Disk Electrode (RRDE) cell 216 containing 5M phosphoric acid, where it was analyzed for ozone concentration in the ozonized water. The flow rate of generated gaseous mixture, the temperature and the voltage of the cell were monitored. All the components shown in Figure 10 were made of Teflon or titanium.

[0082] The cell 206 where electrolysis of water takes place is divided into an anode compartment and a cathode compartment with a cation exchange membrane Nafion117™ separating the two compartments. The anode and cathode were tightly pressed to either side of the ion exchange membrane forming a zero gap cell. A bismuth ruthenium oxide coated

Ti mesh was used as the anode, Nafion 117 with Pt deposited on one surface as the electrolyte and a bare Ti mesh was used as cathode (the bare Ti mesh was in contact with the Pt deposited surface of the Nafion membrane).

**[0083]** The RRDE method was utilized to determine the concentration of the ozone generated. The theory behind the application of RRDE for detection of ozone is briefly as follows. The RRDE consists of a gold disk electrode. The electrode is rotated at a very high speed. This rotational motion sets up a well-defined flow of solution towards the surface of the rotating disk electrode. The flow pattern is akin to a vortex that literally sucks the solution (containing dissolved ozone) towards the electrode. The potential of the disk is controlled by a potentiostat and is slowly swept back and forth across between oxygen and hydrogen evolution. When the disk is cathodically polarized, ozone present in the solution can be quantitatively detected at the disk electrode held at a potential where ozone is reduced. Alternatively the disk is swept in the potential region where the ozone can be reduced. Thus, depending on the amount of ozone present in the electrolyte, the limiting ozone reduction current can be determined. Hence, this method allows comparison of different ozonators for their ozone generation capacity.

**[0084]** EXAMPLE 6

**[0085]** Validity of RRDE Method. To demonstrate the validity of the RRDE analytical method, we used an external ozone-generating device (corona discharge ozonator) to saturate the solution with ozone and performed cyclic voltammetry (CV) of the Au disk after ozonation. Figure 11 shows that ozone is reduced at gold RRDE for potentials more cathodic than 1.0 V vs. SCE. Figure 11 show that oxygen reduction at the ring starts occurring at approximately 0.6 V vs. SCE at room temperature. The presence of ozone gives reduction currents at potentials more cathodic than 1.3 V and a limiting current region can be observed between 0.2V to 1.0 V. Simultaneous reduction of ozone and oxygen takes place at potentials more cathodic than 0.2 V. The main conclusion from Figure 11 is that ozone can be clearly detected at potentials between 0.2 V and 1.0 V and that ozone reduction limiting current is observable between these limits. These results are consistent with other RRDE studies. The limiting ozone reduction current is a direct indicator for the amount of ozone present in the solution.

**[0086]** EXAMPLE 7

**[0087]** Preparation of Anode for the Ozonator. This was done by first preparing an ink with the synthesized  $\text{Bi}_2\text{Ru}_2\text{O}_7$  material prepared according to Example 1. Equal quantities (by weight) of  $\text{Bi}_2\text{Ru}_2\text{O}_7$  material and 5 wt. % Nafion solution (from Aldrich) were

thoroughly mixed to form an ink. The ink was applied to the Pt anode current collector using a brush. The coating was dried in an oven for 1 hour at 130° C to remove all the organics from the Nafion solution. Multiple coatings were applied in this manner to make a uniform coating of  $\text{Bi}_2\text{Ru}_2\text{O}_7$  material on the Pt substrate. The coated anode was rehydrated by allowing it to soak it in distilled water overnight.

**[0088]** EXAMPLE 8

**[0089]** Operation of Ozonator with Bismuth Ruthenium Oxide Anode. The  $\text{Bi}_2\text{Ru}_2\text{O}_7$  coated Pt anode current collector prepared according to Example 7 was used as the anode in the ozonator in the place of Pt or  $\text{PbO}_2$ . The performance of the  $\text{Bi}_2\text{Ru}_2\text{O}_7$  cell is shown in Figure 12. The initial ozone current is 70  $\mu\text{A}$  (compared to 80  $\mu\text{A}$  recorded with  $\text{PbO}_2$  cell built and operated in similar fashion). However, the ozone current decreased to about 30  $\mu\text{A}$  in about 2 hrs. This steep decline in ozone current can be attributed to (1) loss of  $\text{Bi}_2\text{Ru}_2\text{O}_7$  material or (2) clogging of the Nafion membrane or (3) loss of contact between the coating and the current collector.

**[0090]** The platinum anode current collector was used as a substrate for the bismuth ruthenium oxide coating in the above experiment. It is possible that ozone is being generated by the platinum anode current collector and not the bismuth ruthenium oxide material. In order to prove that is not the case, the  $\text{Bi}_2\text{Ru}_2\text{O}_7$  material was coated on a Ti mesh on top of the Pt anode current collector as the anode. First, the cell was assembled with bare titanium mesh on top of the Pt anode current collector. The cell could not be operated (30A current could not be sustained) with this setup. Then the cell was assembled with  $\text{Bi}_2\text{Ru}_2\text{O}_7$  material coated Ti mesh in the place of bare Ti mesh. This time the cell could be operated and the resulting data are shown in Figure 13. An initial ozone current of 13  $\mu\text{A}$  was recorded that reached to 23  $\mu\text{A}$  in about 1 hour of operation and slowly decreased to 17  $\mu\text{A}$  in about 4.5 hours of operation. The fact that ozone was being generated in this experiment implies that  $\text{Bi}_2\text{Ru}_2\text{O}_7$  material is responsible for it and not the Pt anode current collector. The cell voltage and temperature were stabilized at 13.5 V and 33°C respectively. These values are higher than those recorded for the experiment that used  $\text{Bi}_2\text{Ru}_2\text{O}_7$  coated Pt anode current collector as the anode. This could be due to enhanced interfacial resistances when Ti mesh was used.

**[0091]** The foregoing experiments show that ozone may be generated by a  $\text{Bi}_2\text{Ru}_2\text{O}_7$  pyrochlore anode in the ozonator. While the examples focus on  $\text{Bi}_2\text{Ru}_2\text{O}_7$  as one suitable electrode material for the electrolytic ozone generation, the invention is not limited to

Bi<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub>. Other Bi based pyrochlores with Ir, Sn, Rh, Pt and Ti can also be potentially used and are within the scope of the disclosed invention. These bismuth pyrochlore materials are attractive electrode materials for electrolytic ozone or perchlorate generation.

[0092] While specific embodiments and examples of the present invention have been illustrated and described, numerous modifications come to mind without significantly departing from the spirit of the invention, and the scope of protection is only limited by the scope of the accompanying claims.

## CLAIMS:

1. An electrolytic method of generating ozone comprising:  
providing an electrolytic cell having an anode comprising a bismuth mixed metal oxide pyrochlore material having the general formula  $A_2B_2O_{7-x}$ , where A is Bi and B is Ru, Ir, Rh, Sn, Ti, or Pt, and  $0 \leq x \leq 1$ ; and  
operating the electrolytic cell anode at a current density sufficient to generate ozone.
2. The method of claim 1, wherein the generation of ozone is accomplished according to the reaction:  $3H_2O \rightarrow O_3 + 6H^+ + 6e^-$ .
3. The method of claim 1, wherein the electrolytic cell anode is operated at a current density greater than about  $1 \text{ A/cm}^2$ .
4. The method of claim 1, wherein the electrolytic cell anode is operated at a current density greater than about  $1.2 \text{ A/cm}^2$ .
5. The method of claim 1, wherein the electrolytic cell anode is operated at a current density greater than about  $1.4 \text{ A/cm}^2$ .
6. The method of claim 1, wherein the electrolytic cell anode is operated at a current density of approximately  $1.5 \text{ A/cm}^2$ .
7. The method of claim 1, wherein B is Ru.
8. The method of claim 1, wherein the electrolytic cell has a cathode comprising the bismuth mixed metal oxide pyrochlore material.
9. The method of claim 1, wherein the anode comprises a composite of the bismuth mixed metal oxide pyrochlore material and one or more noble metals selected from Pt, Ag, Au, Ru, Re, and Pd.
10. An electrolytic cell for generating ozone comprising:  
an anode comprising a bismuth mixed metal oxide pyrochlore material having the general formula  $A_2B_2O_{7-x}$ , where A is Bi and B is Ru, Ir, Rh, Sn, Ti, or Pt, and  $0 \leq x \leq 1$ ;  
a cathode;  
electrolyzable water in contact with the anode and the cathode; and  
a source of electric potential and current electrically coupled to the anode and the cathode to produce an operating current density sufficient to generate ozone at the anode.
11. The method of claim 1, wherein the generation of ozone is accomplished according to the reaction:  $3H_2O \rightarrow O_3 + 6H^+ + 6e^-$ .
12. The electrolytic cell of claim 10, wherein the electrolytic cell anode is operated at a current density greater than about  $1 \text{ A/cm}^2$ .



13. The electrolytic cell of claim 10, wherein the electrolytic cell anode is operated at a current density greater than about  $1.2 \text{ A/cm}^2$ .

14. The electrolytic cell of claim 10, wherein the electrolytic cell anode is operated at a current density greater than about  $1.4 \text{ A/cm}^2$ .

15. The electrolytic cell of claim 10, wherein the electrolytic cell anode is operated at a current density of approximately  $1.5 \text{ A/cm}^2$ .

16. The electrolytic cell of claim 10, wherein B is Ru.

17. The electrolytic cell of claim 10, wherein the electrolytic cell has a cathode comprising the bismuth mixed metal oxide pyrochlore material.

18. The electrolytic cell of claim 10, wherein the anode comprises a composite of the bismuth mixed metal oxide pyrochlore material and one or more noble metals selected from Pt, Ag, Au, Ru, Re, and Pd.

19. An electrolytic method of generating a perchlorate salt comprising:  
providing an electrolytic cell having an anode comprising a bismuth mixed metal oxide pyrochlore material having the general formula  $\text{A}_2\text{B}_2\text{O}_{7-x}$ , where A is Bi and B is Ru, Ir, Rh, Sn, Ti, or Pt, and  $0 \leq x \leq 1$ ; and

operating the electrolytic cell anode at a current density sufficient to oxidize a chlorate salt in aqueous solution to form a perchlorate salt in aqueous solution.

20. The method of claim 19, wherein the electrolytic cell anode is operated at a current density greater than about  $1 \text{ A/cm}^2$ .

21. The method of claim 19, wherein B is Ru.

22. The method of claim 19, wherein the electrolytic cell has a cathode comprising the bismuth mixed metal oxide pyrochlore material.

23. The method of claim 19, wherein the anode comprises a composite of the bismuth mixed metal oxide pyrochlore material and one or more noble metals selected from Pt, Ag, Au, Ru, Re, and Pd.

24. An electrolytic cell for generating a perchlorate salt comprising:  
an anode comprising a bismuth mixed metal oxide pyrochlore material having the general formula  $A_2B_2O_{7-x}$ , where A is Bi and B is Ru, Ir, Rh, Sn, Ti, or Pt, and  $0 \leq x \leq 1$ ;  
a cathode;  
a chlorate salt in aqueous solution in contact with the anode; and  
a source of electric potential and current electrically coupled to the anode and the cathode to produce an operating current density sufficient to oxidize a chlorate salt in aqueous solution to form a perchlorate salt in aqueous solution at the anode.
25. The electrolytic cell of claim 24, wherein B is Ru.
26. The electrolytic cell of claim 24, wherein the electrolytic cell has a cathode comprising the bismuth mixed metal oxide pyrochlore material.
27. The electrolytic cell of claim 24, wherein the anode comprises a composite of the bismuth mixed metal oxide pyrochlore material and one or more noble metals selected from Pt, Ag, Au, Ru, Re, and Pd.

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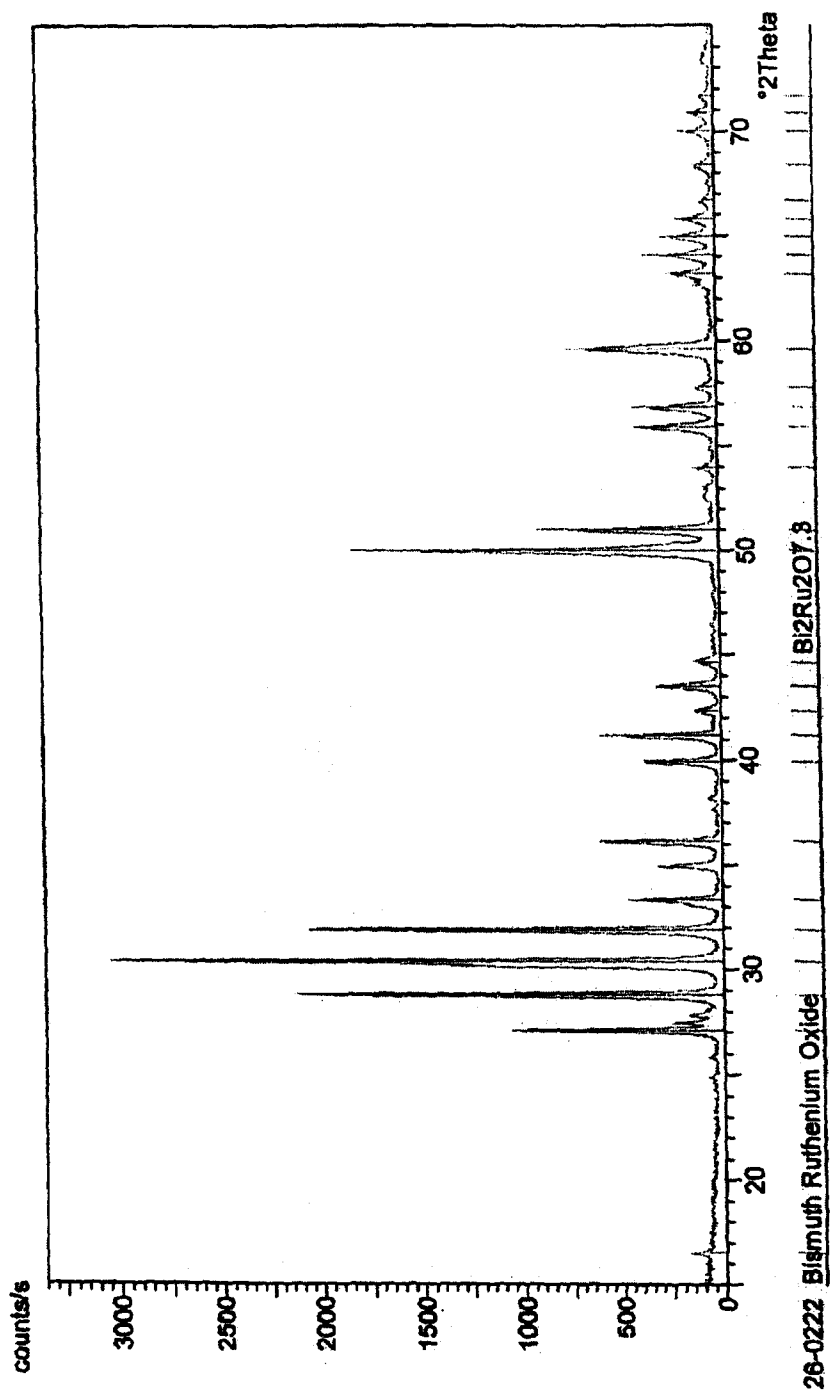


Fig. 1

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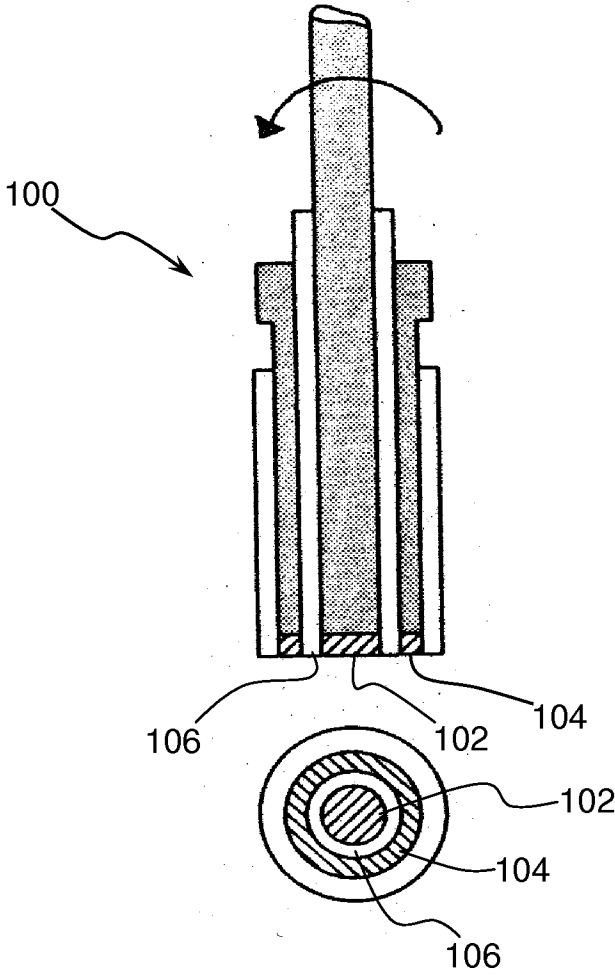


Fig. 2

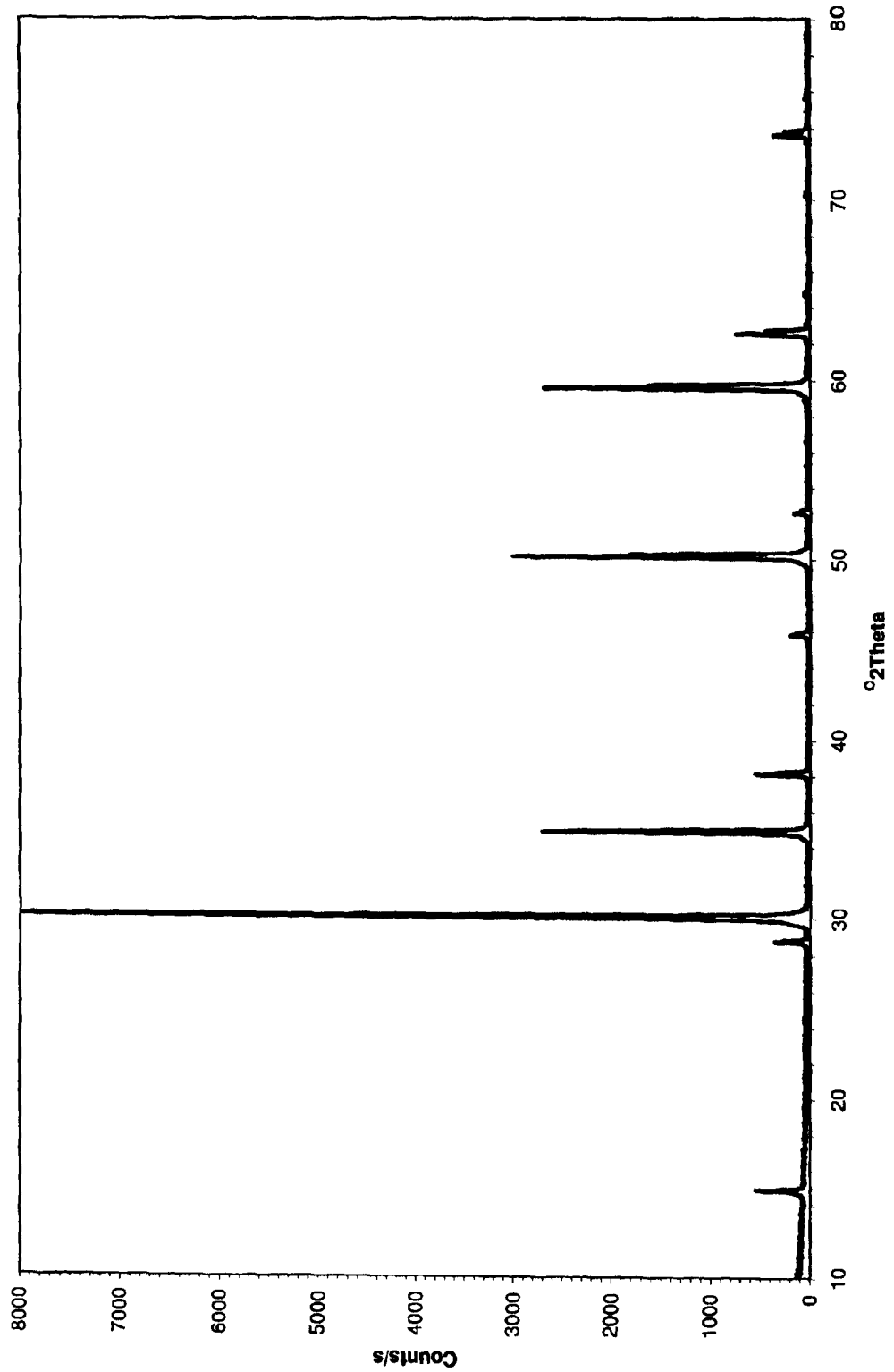


Fig. 3

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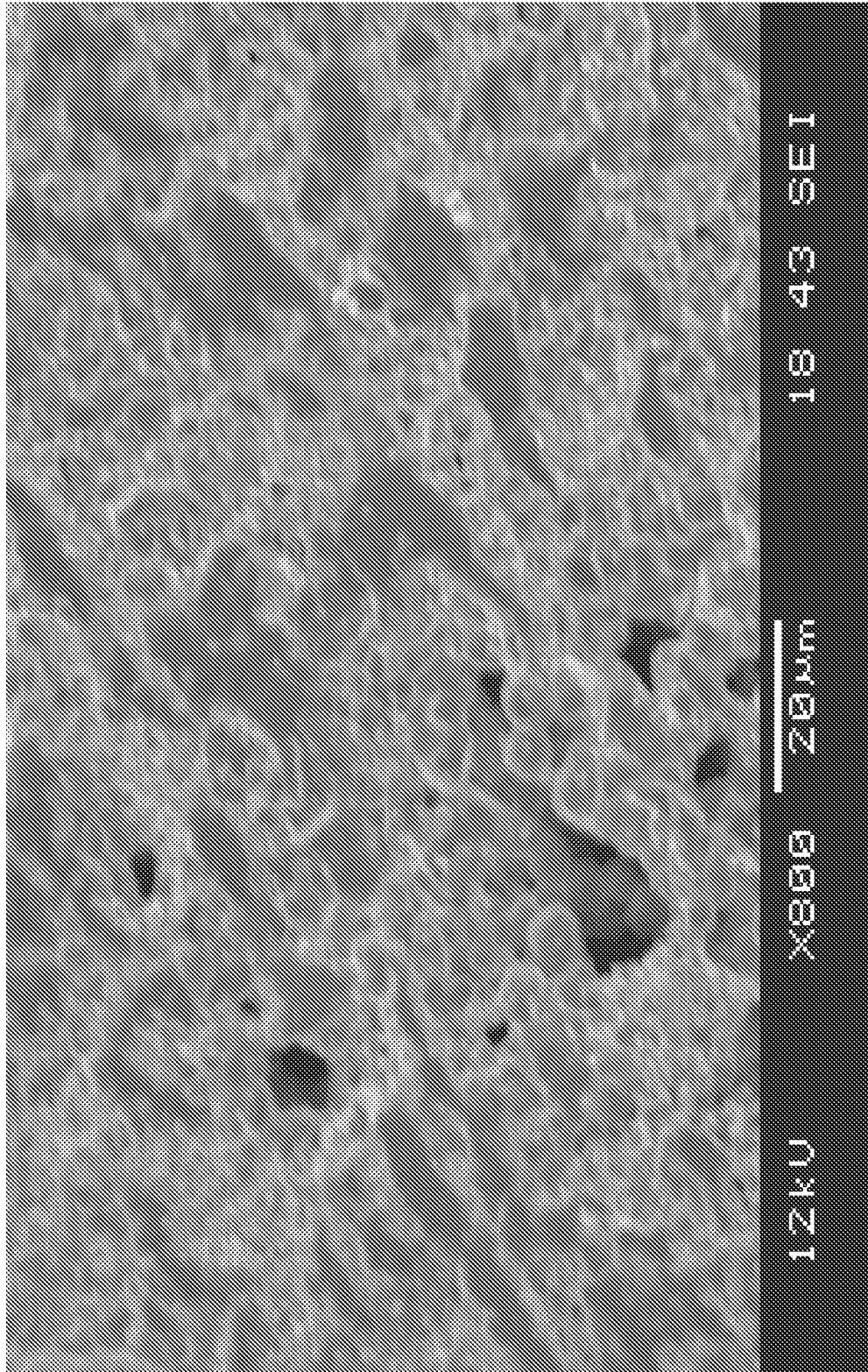


Fig. 4

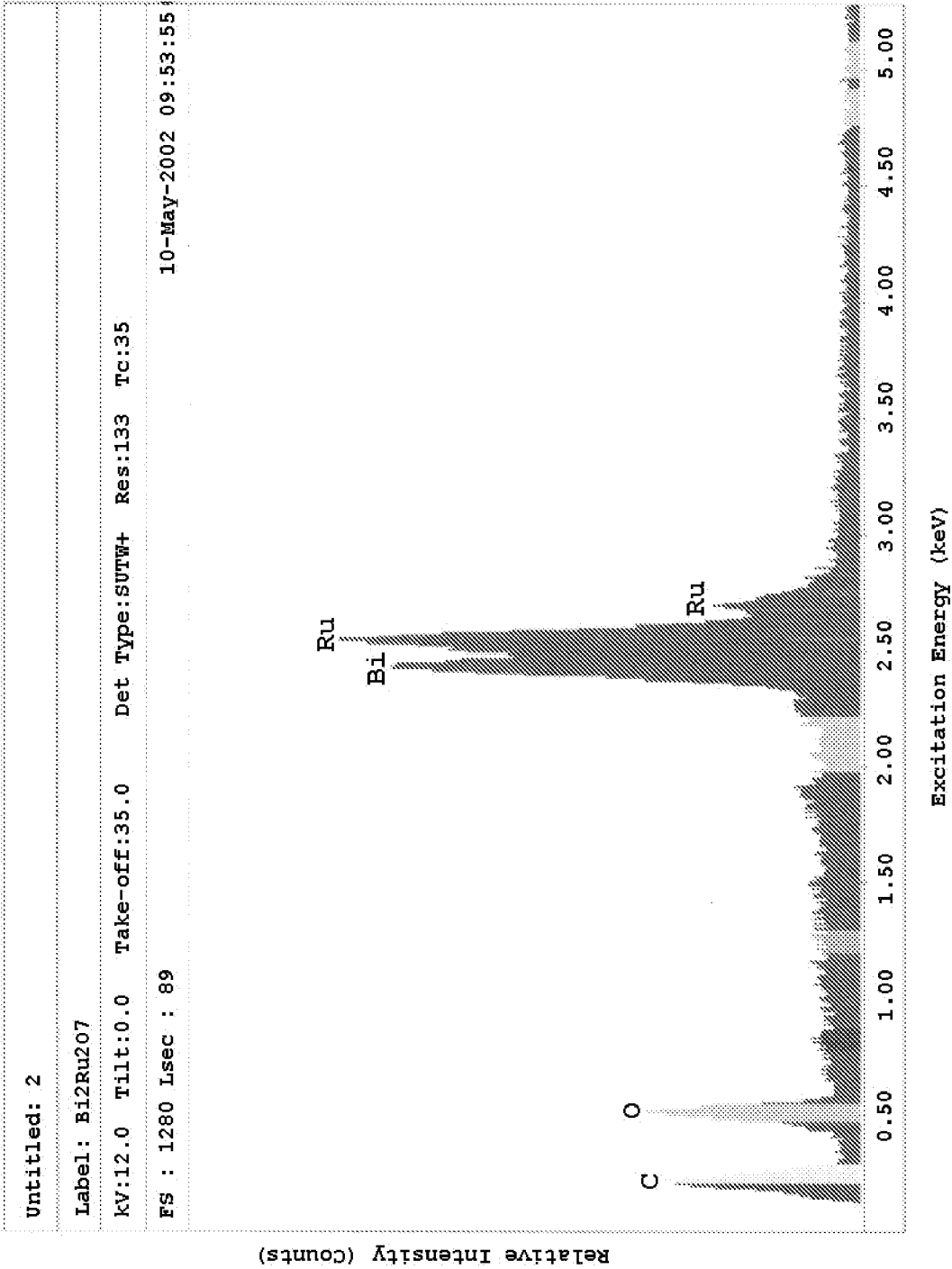


Fig. 5

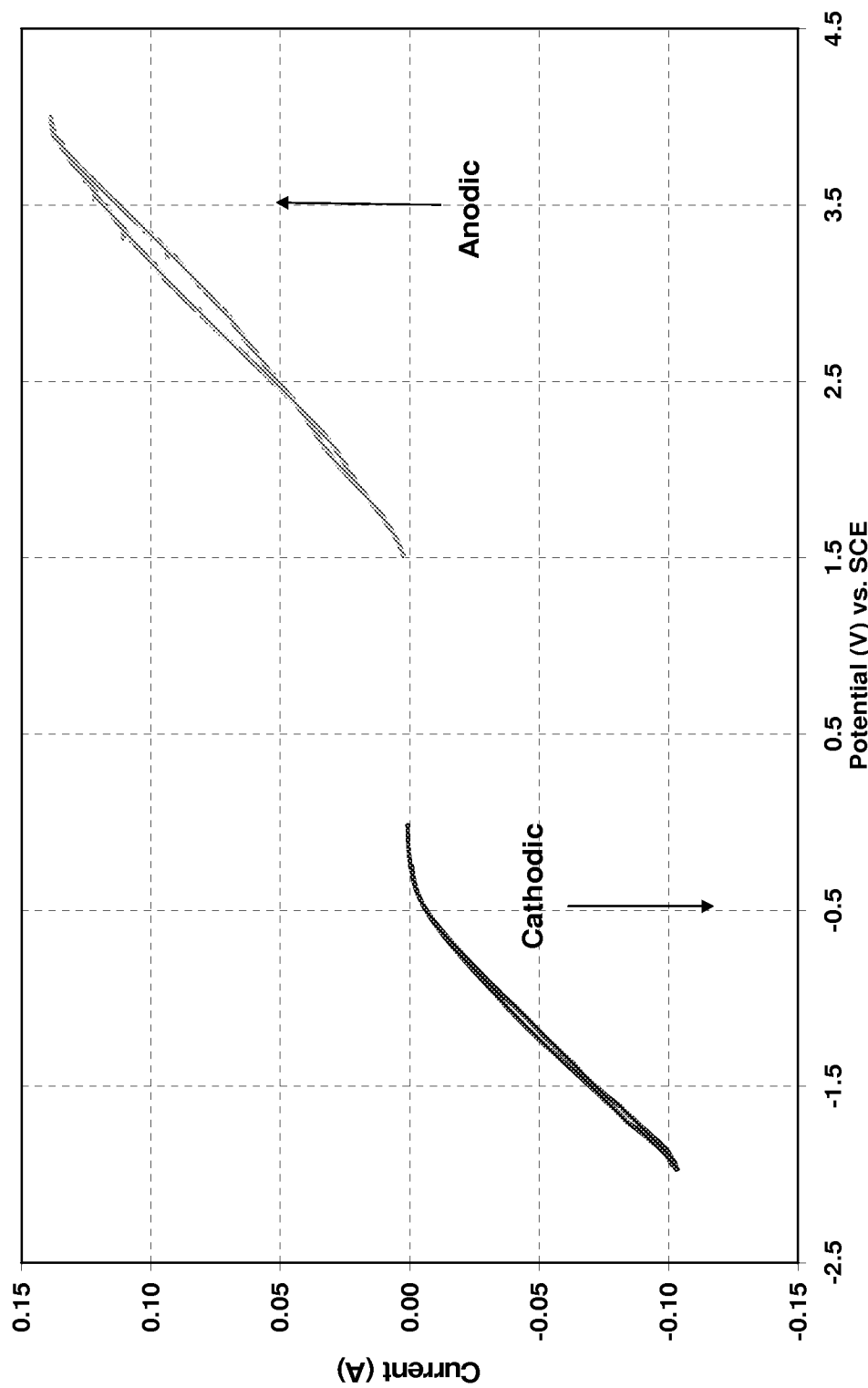


Fig. 6



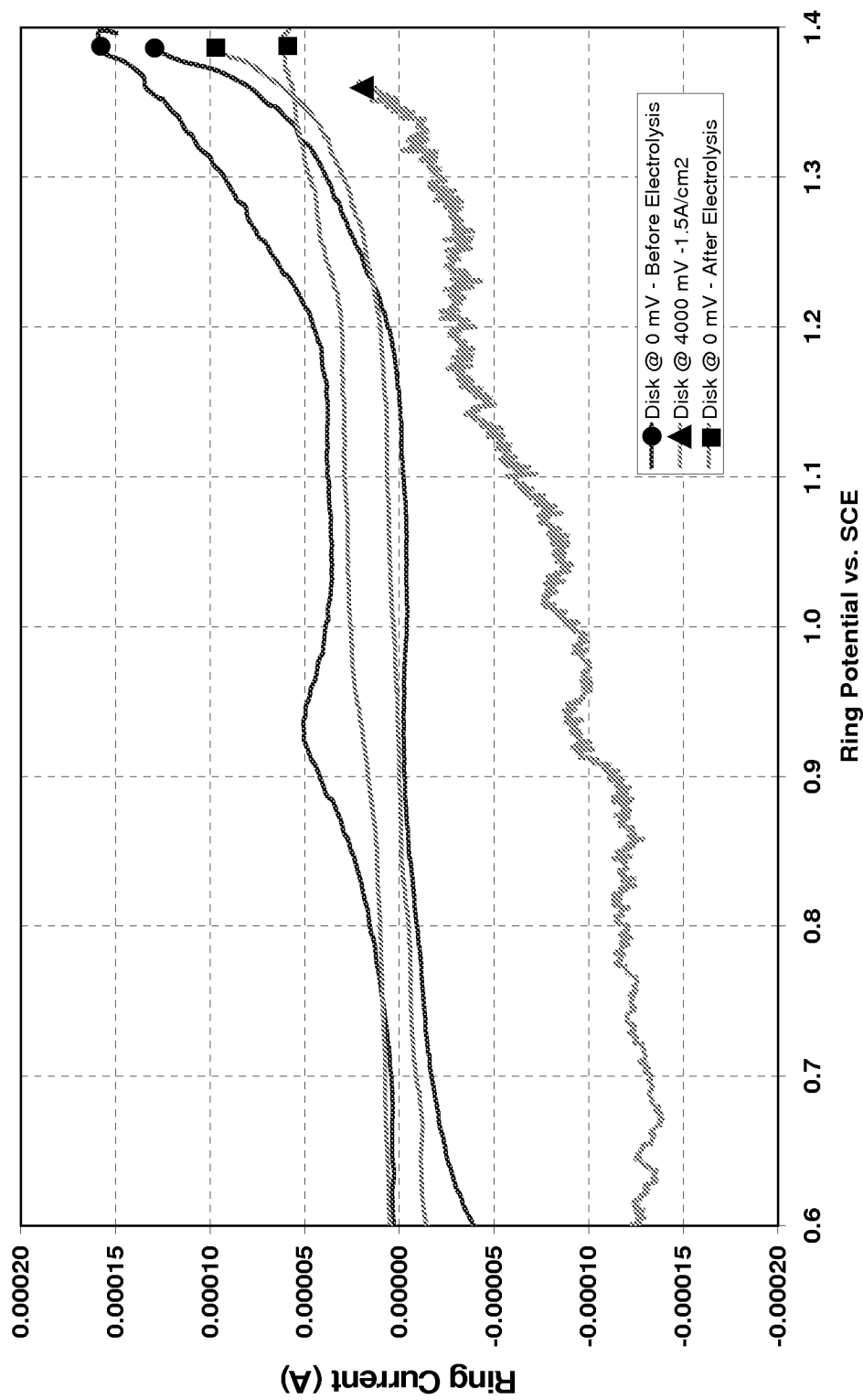


Fig. 7

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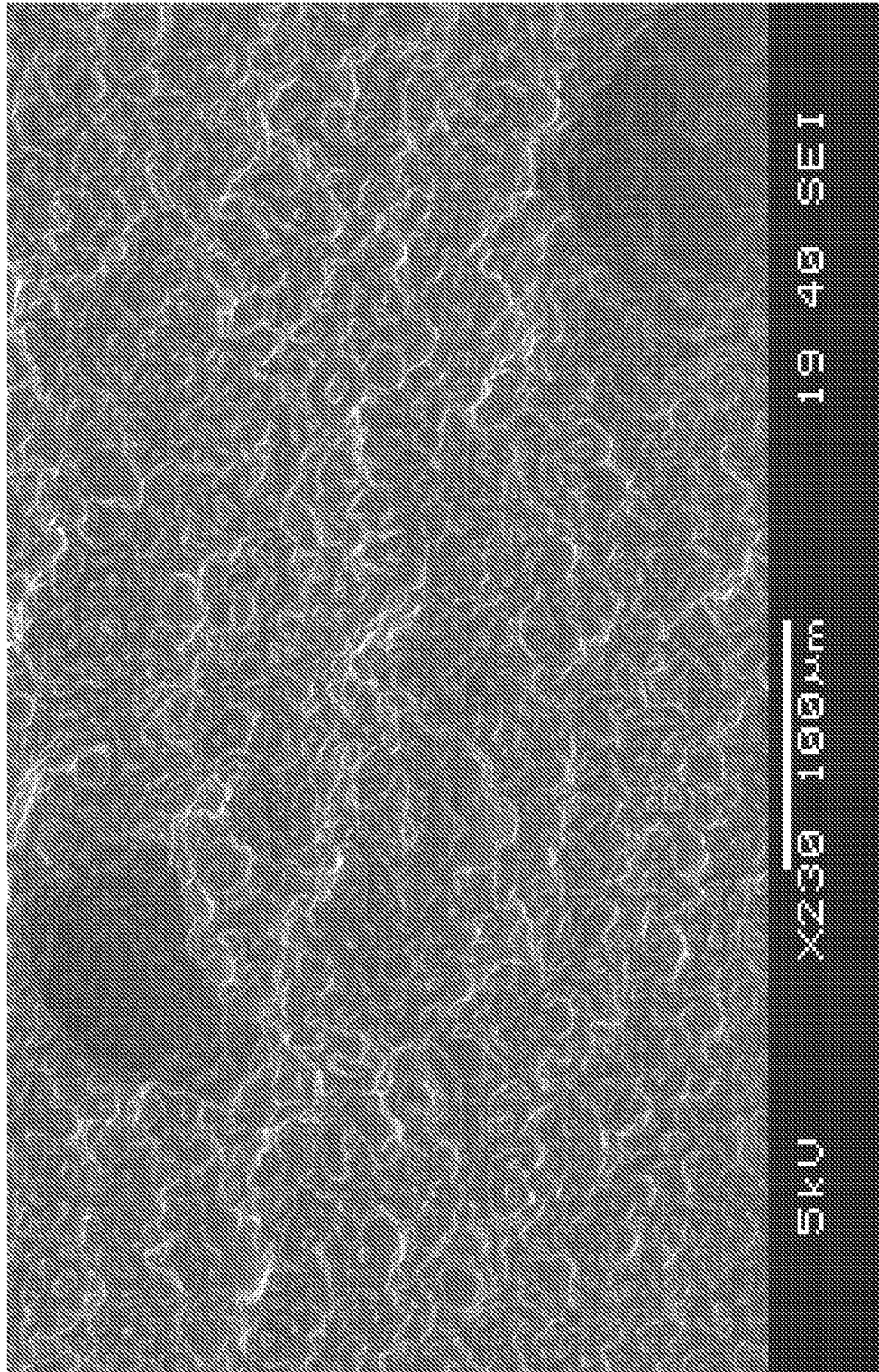


Fig. 8

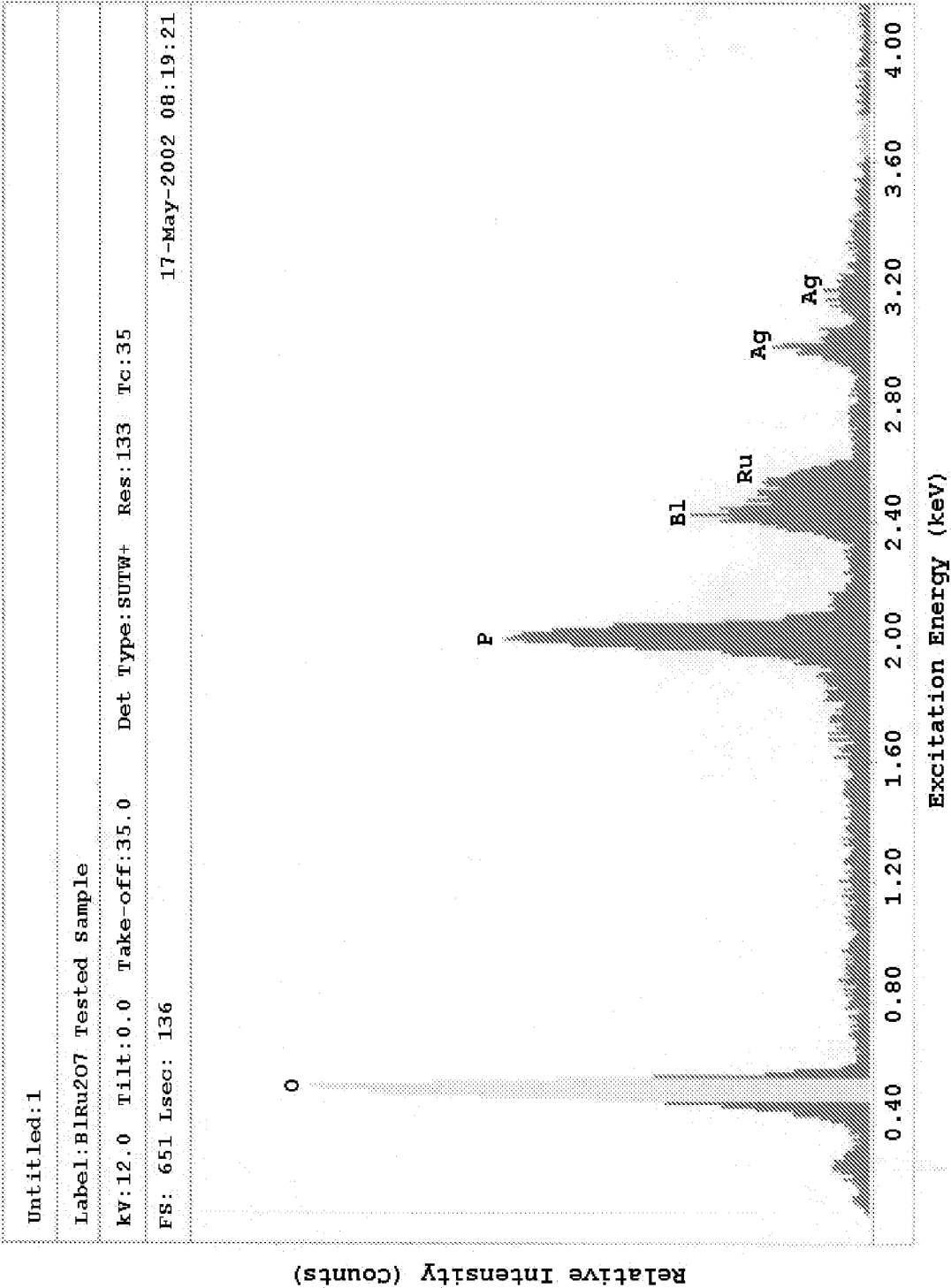


Fig. 9

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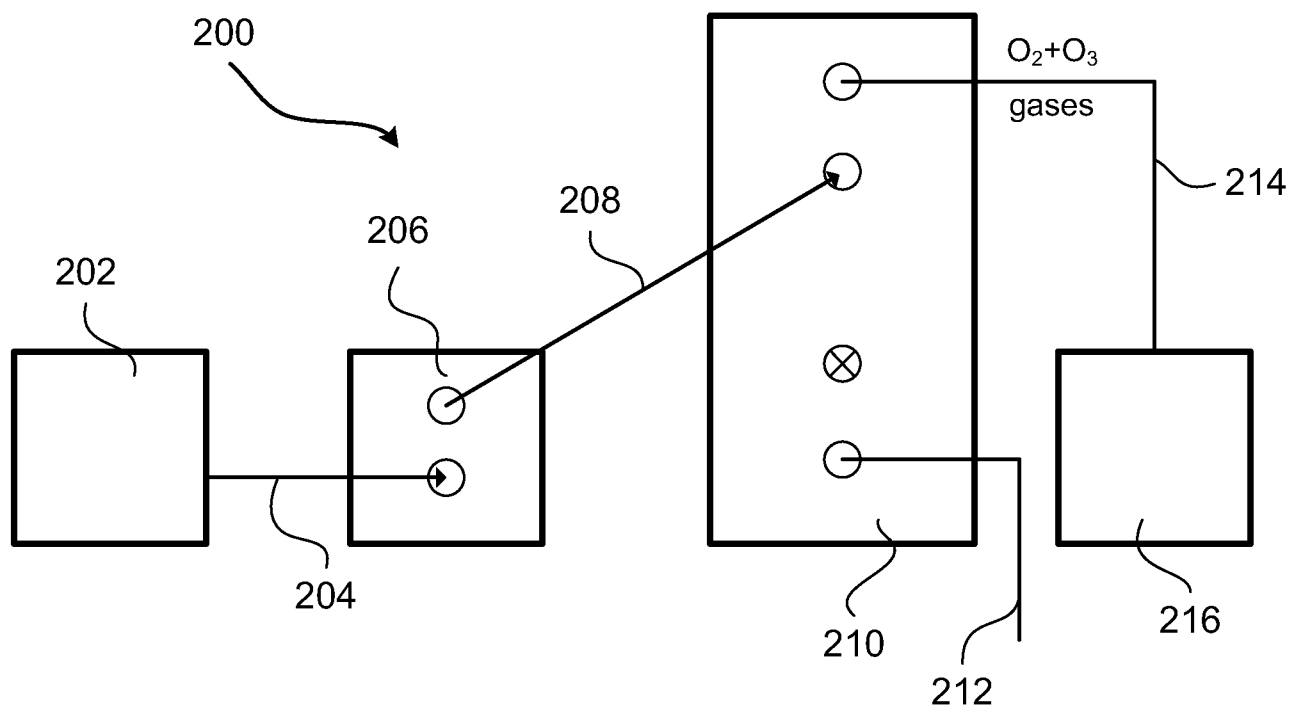


Fig. 10

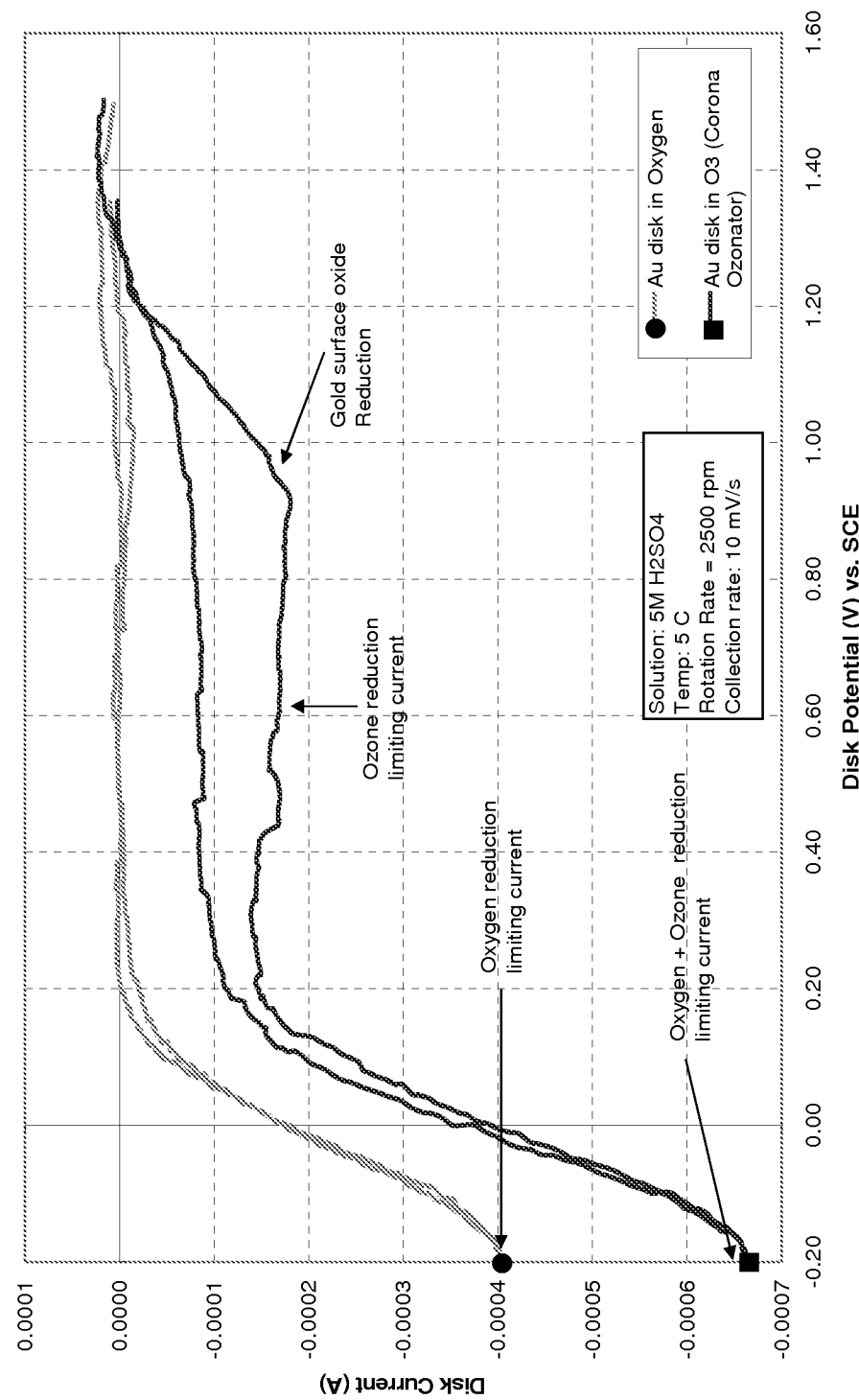


Fig. 11

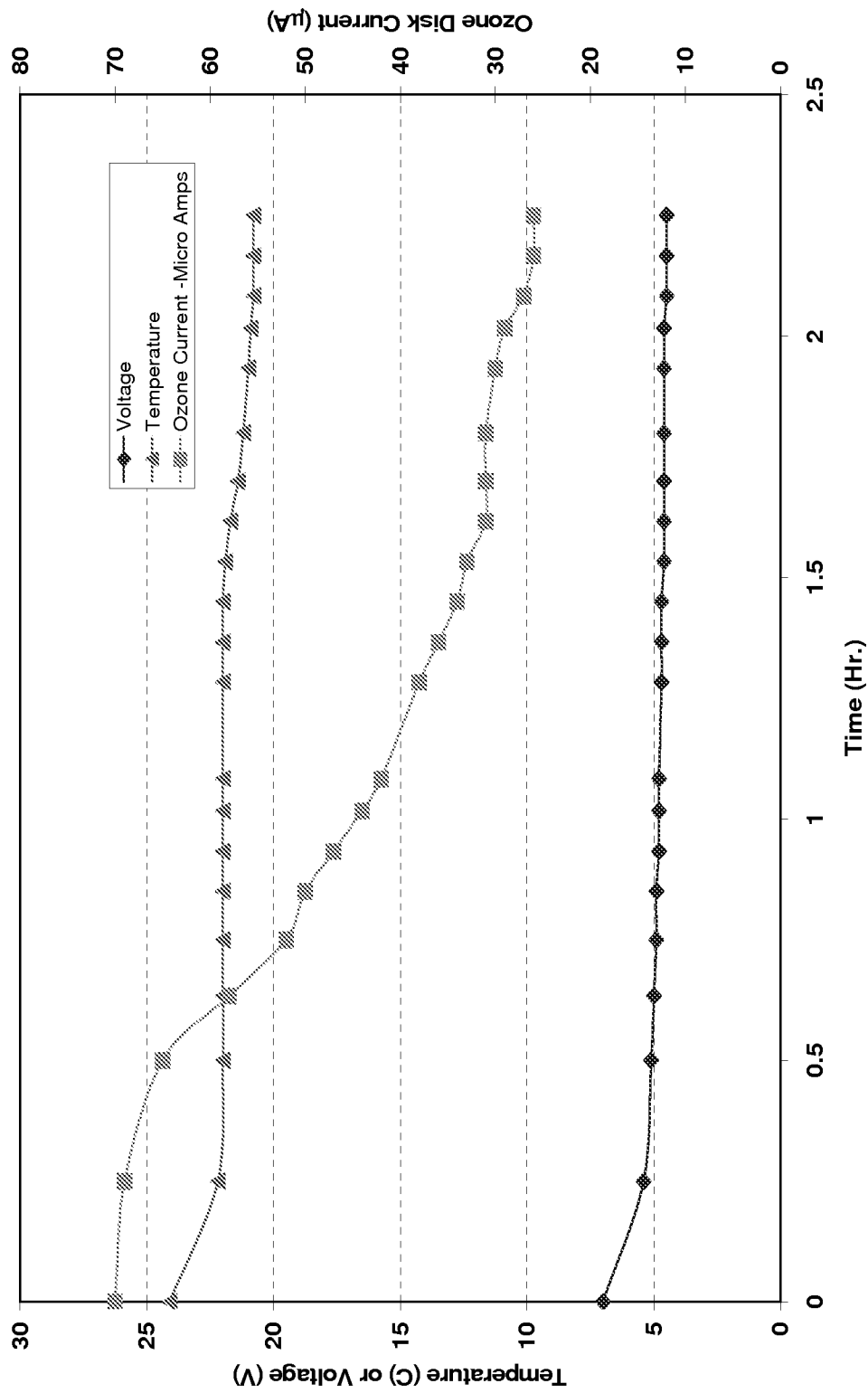


Fig. 12

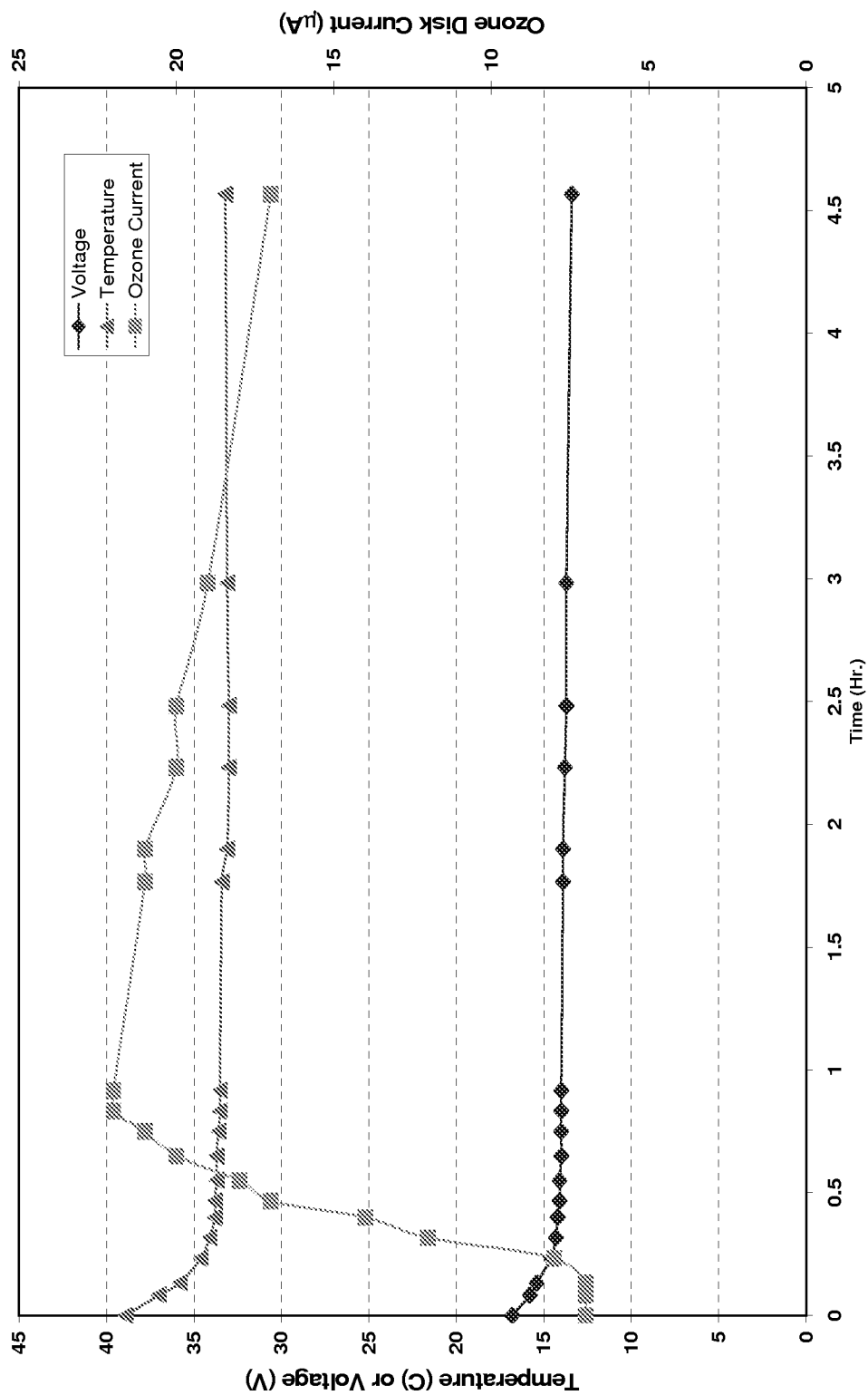


Fig. 13