



(54) **ELECTROCHEMICAL MODULATION OF THE FLAMMABILITY OF IONIC LIQUID FUELS**

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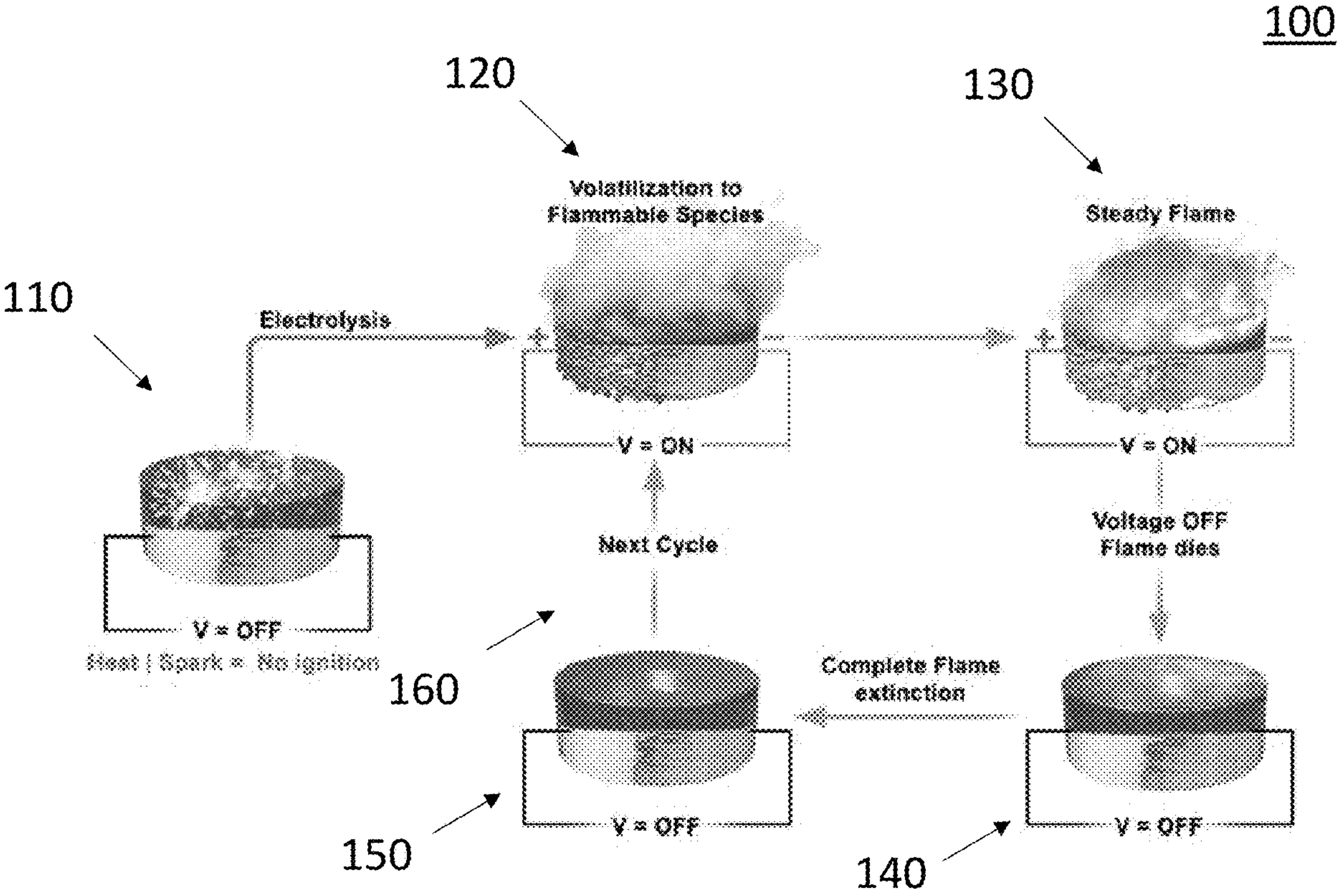
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(57) **ABSTRACT**

A method, a system, and a non-transitory computer-readable medium for controlling flammability of a fuel. The method includes applying a voltage across a nonvolatile ionic liquid to convert the nonvolatile ionic liquid into a flammable liquid; and removing the applied voltage across the non-volatile ionic liquid to revert the flammable liquid back to the nonvolatile ionic liquid.



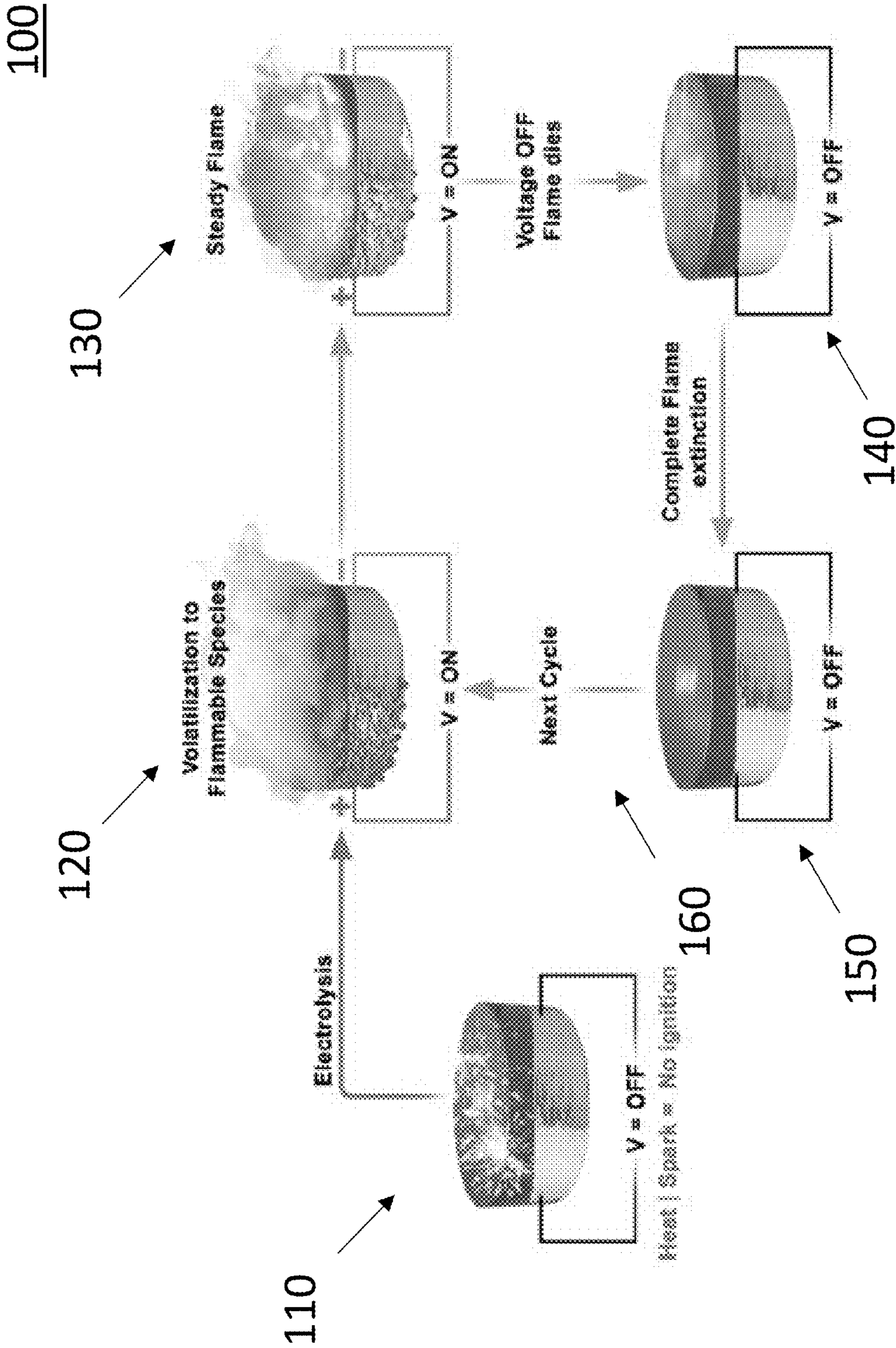


FIG. 1

FIG. 2A

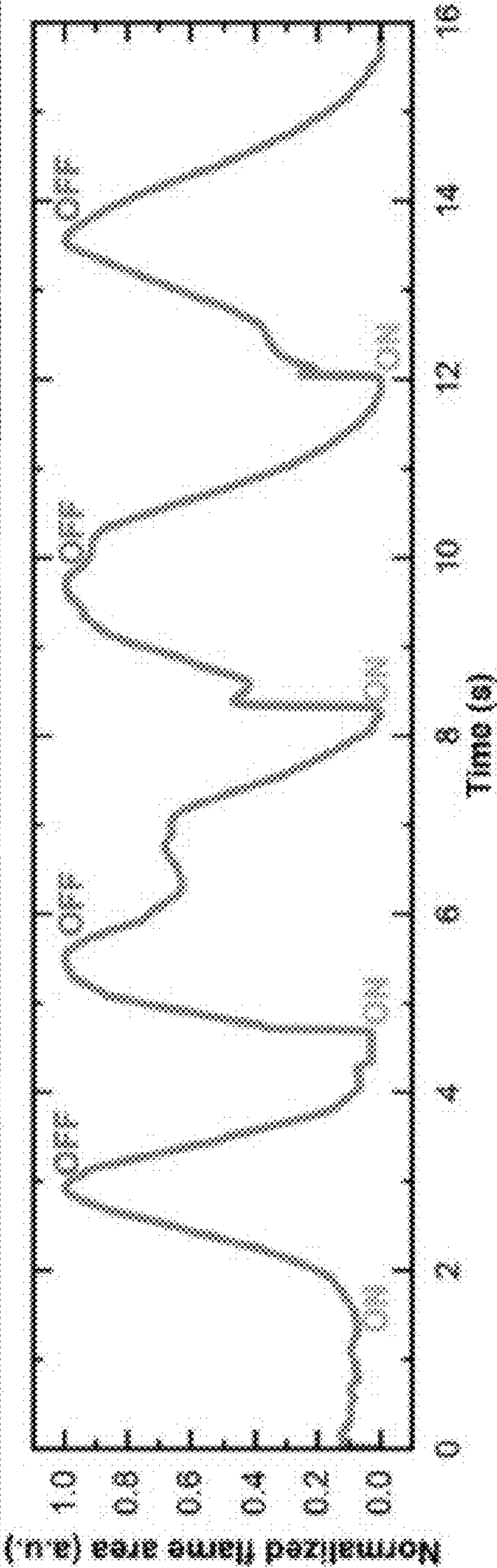
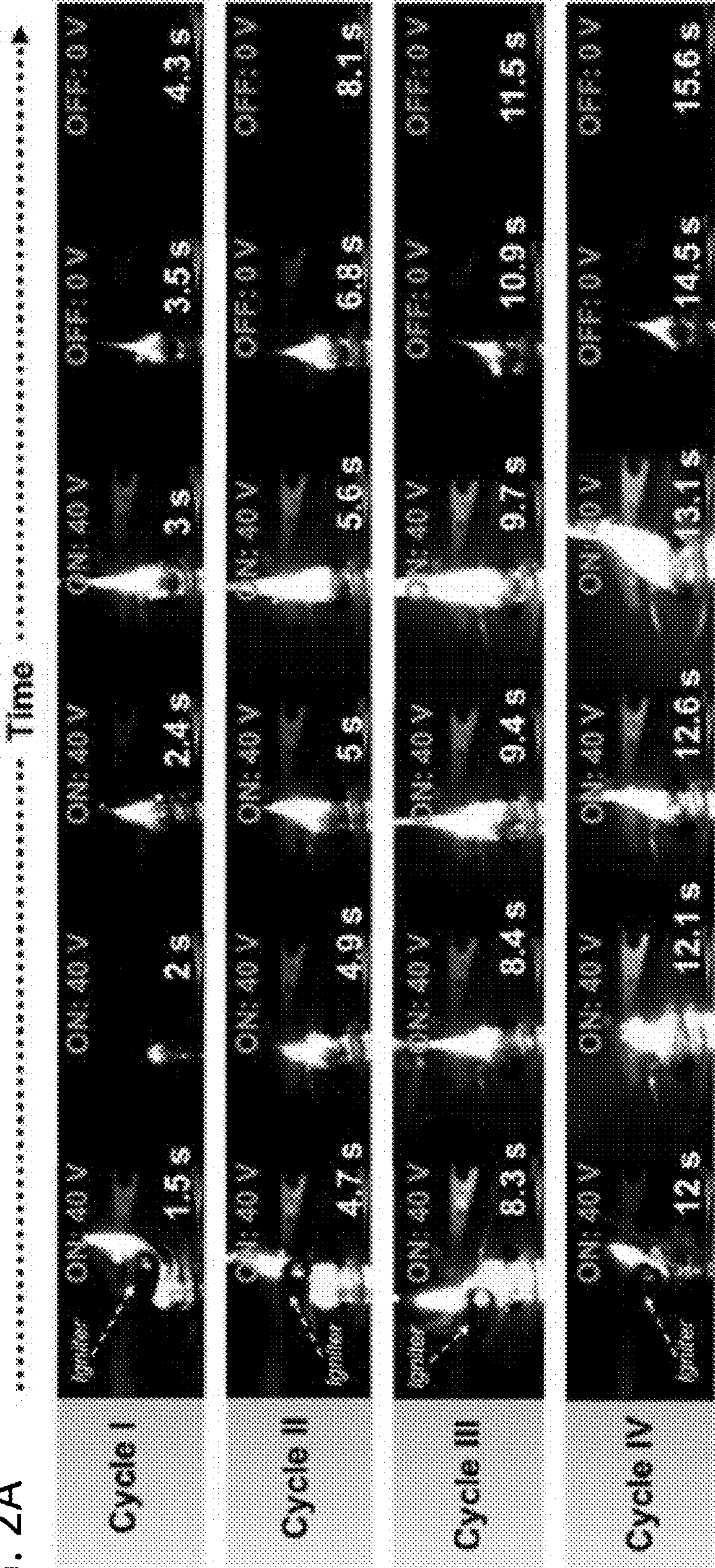


FIG. 2B

FIG. 3A

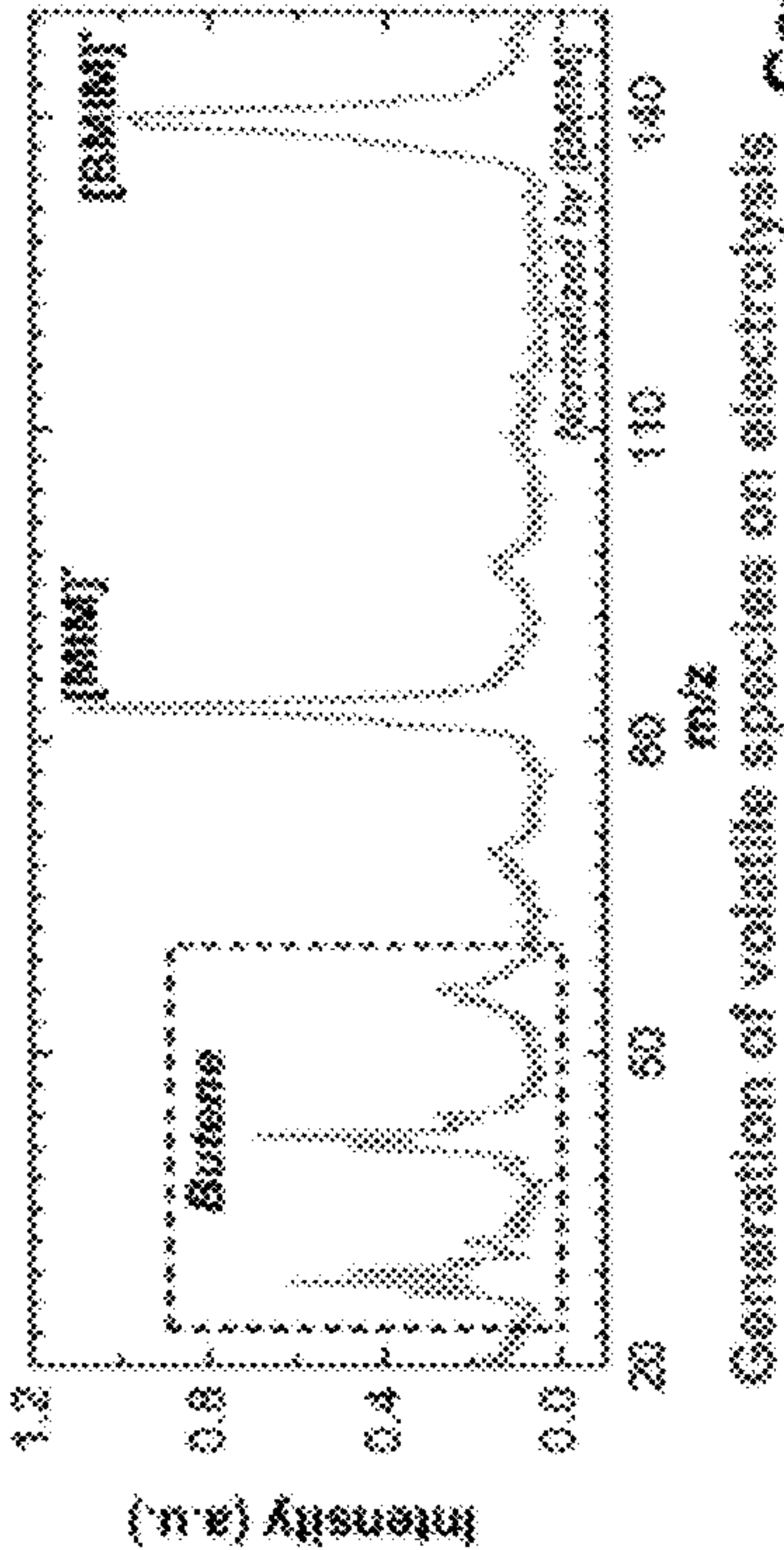


FIG. 3C

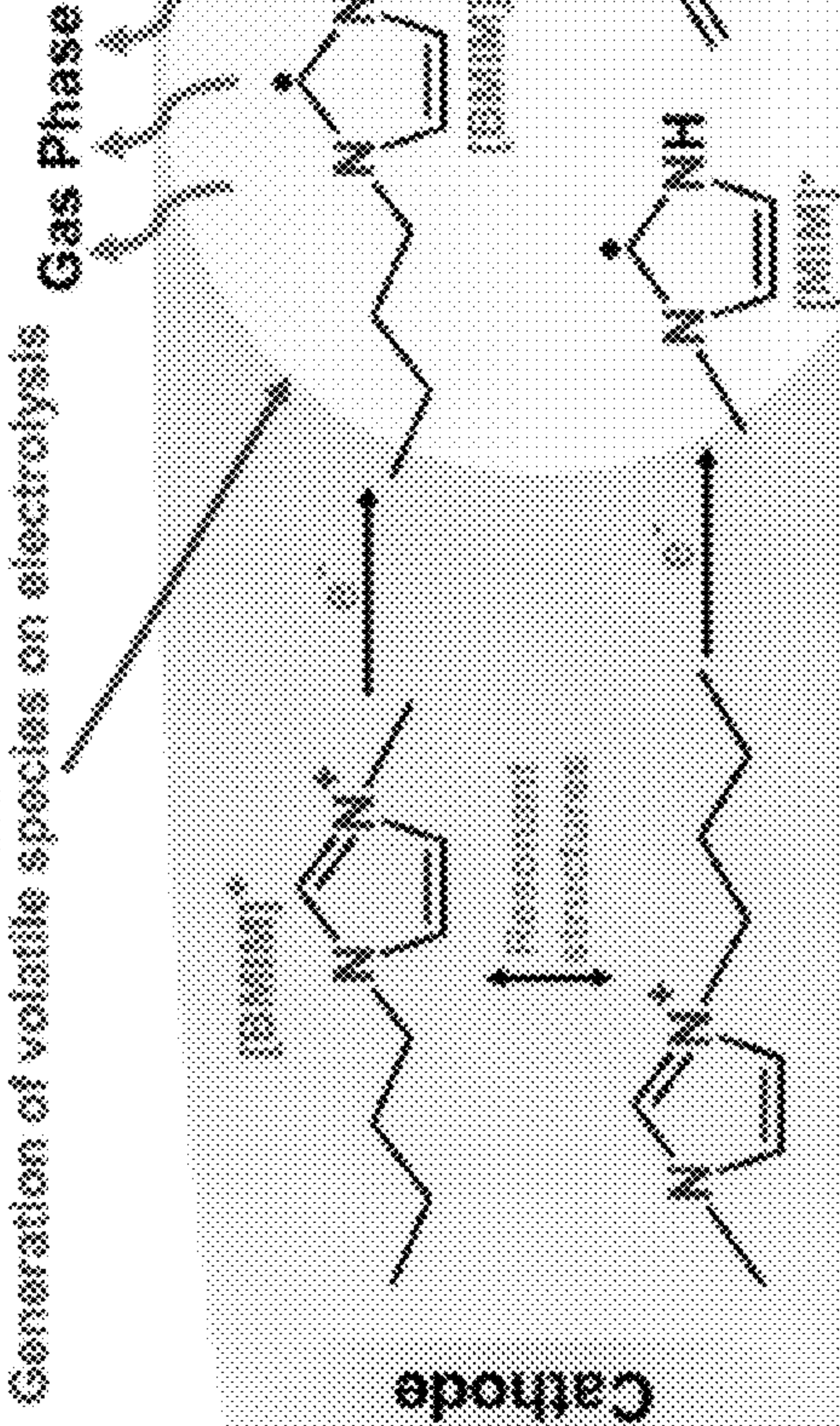
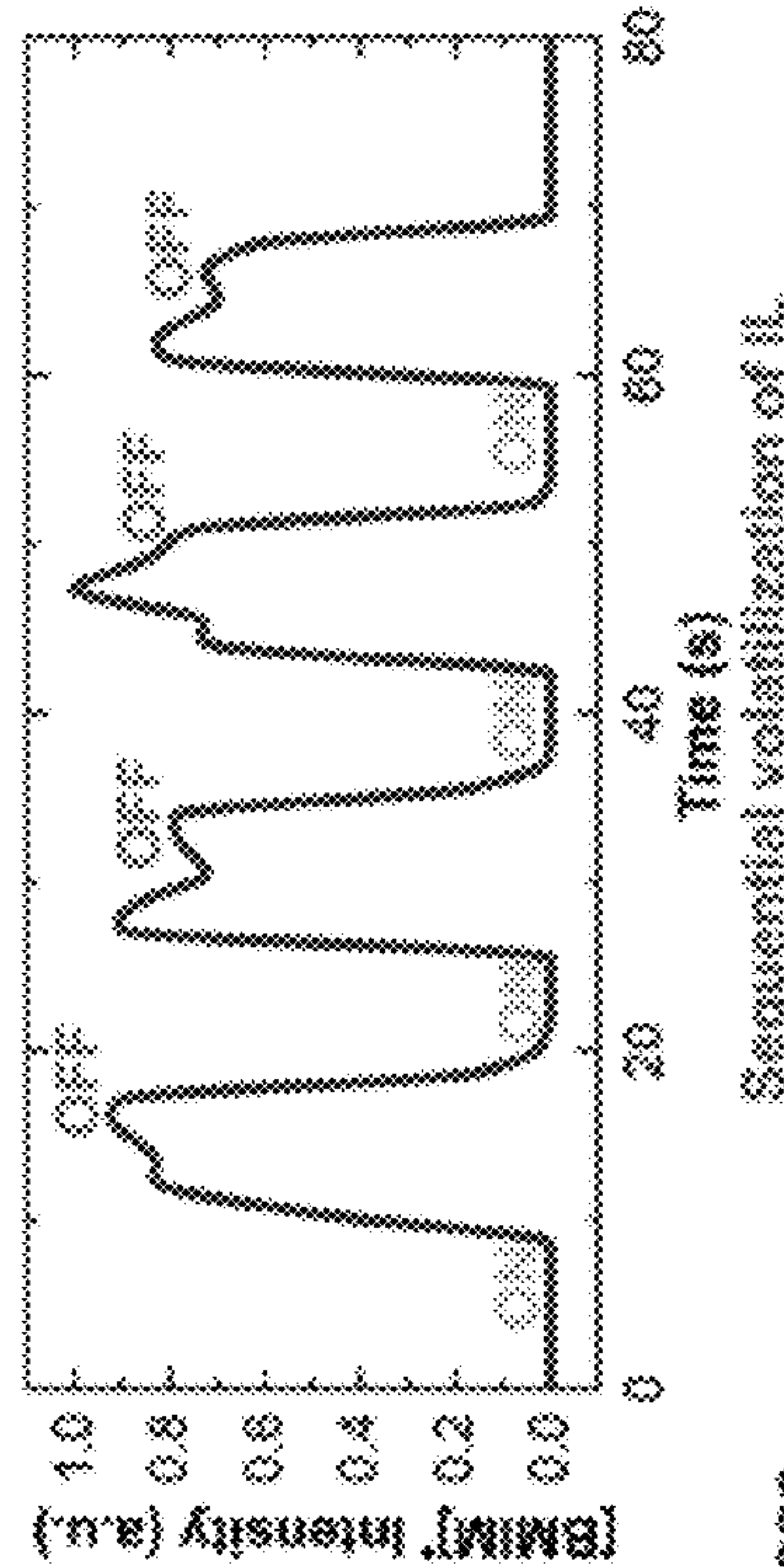


FIG. 3B

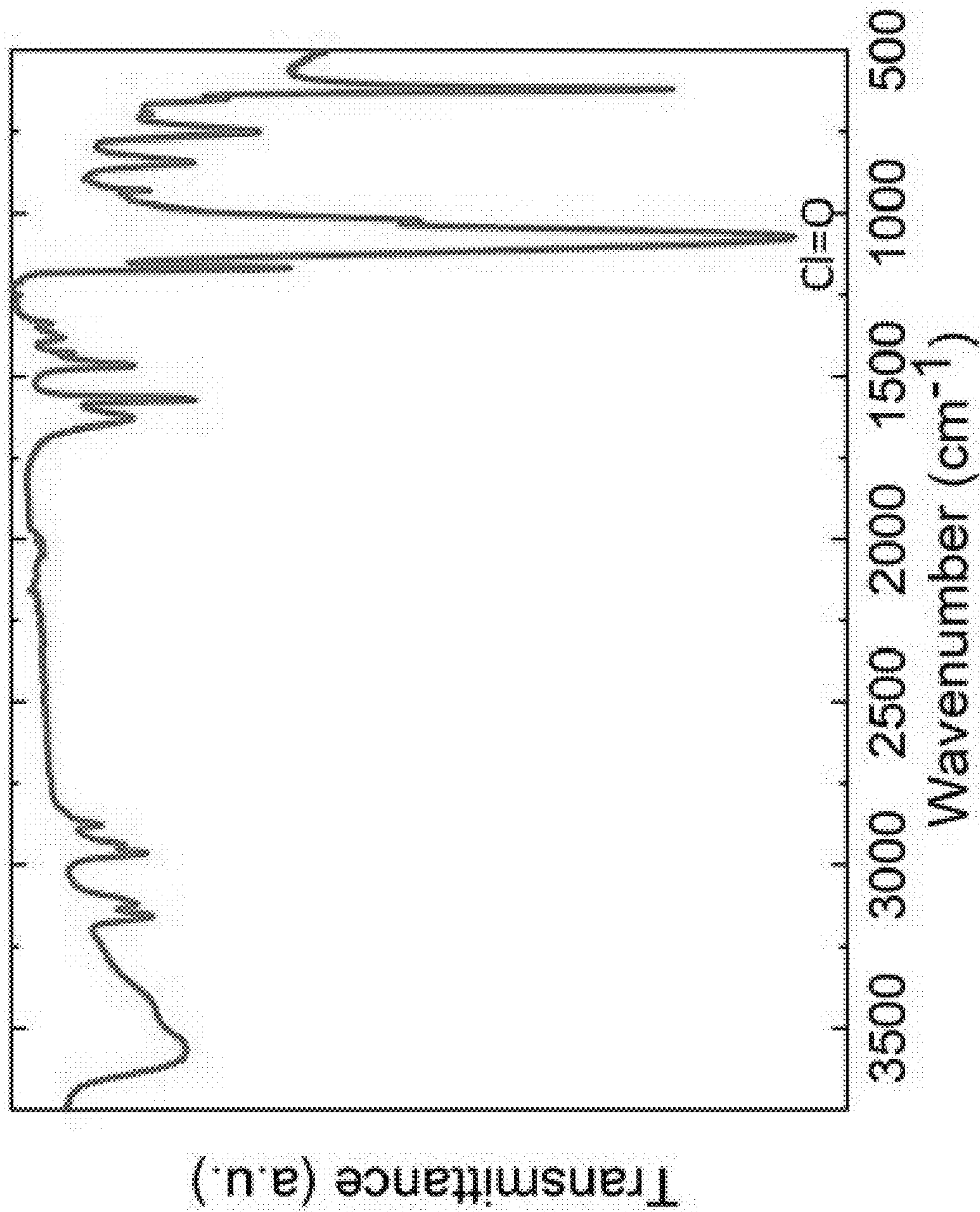


FIG. 4

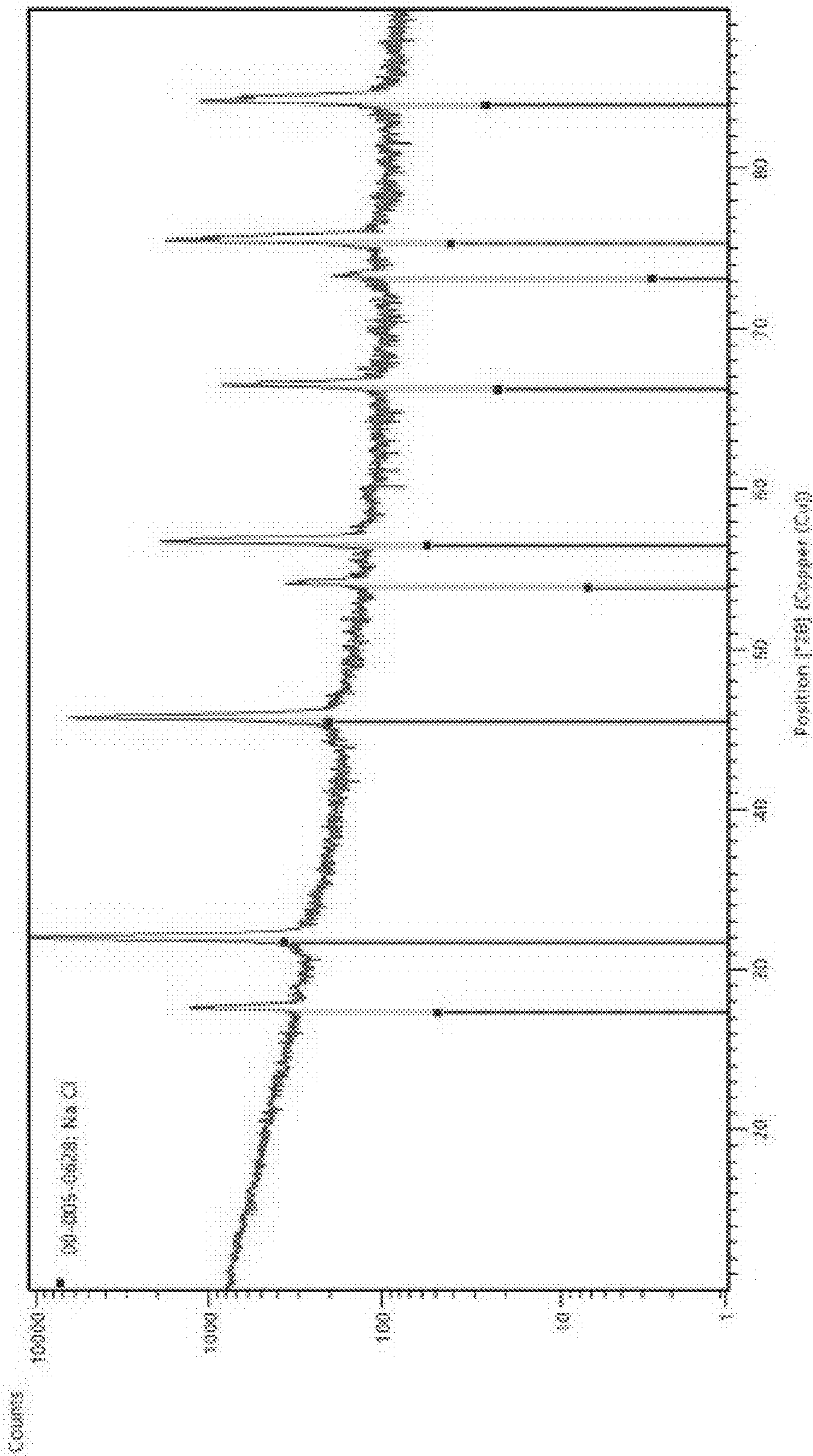


FIG. 5

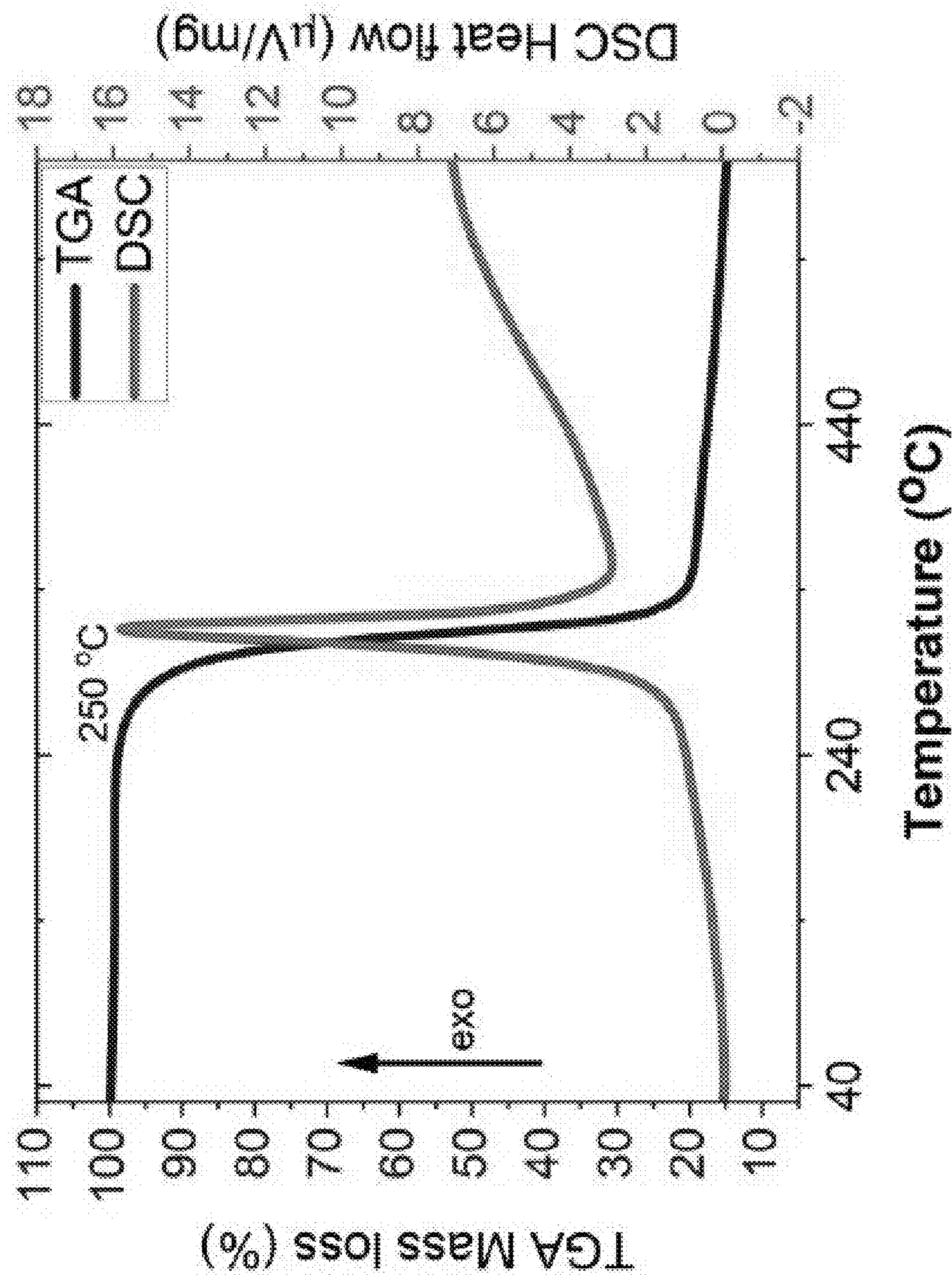


FIG. 6

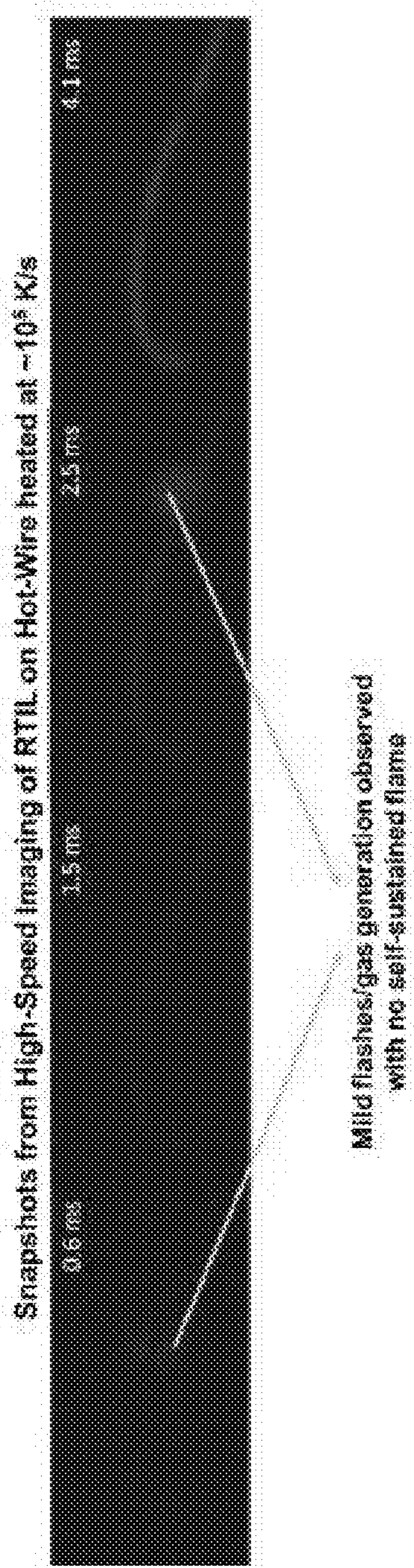


FIG. 7

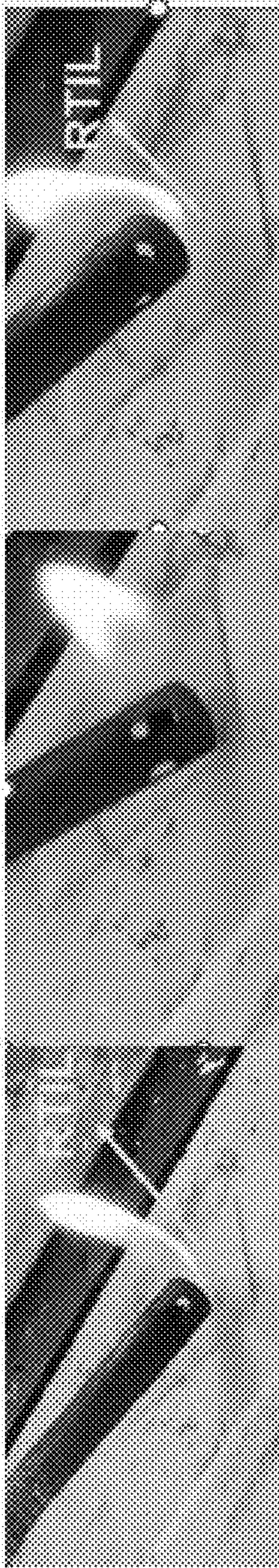


FIG. 8

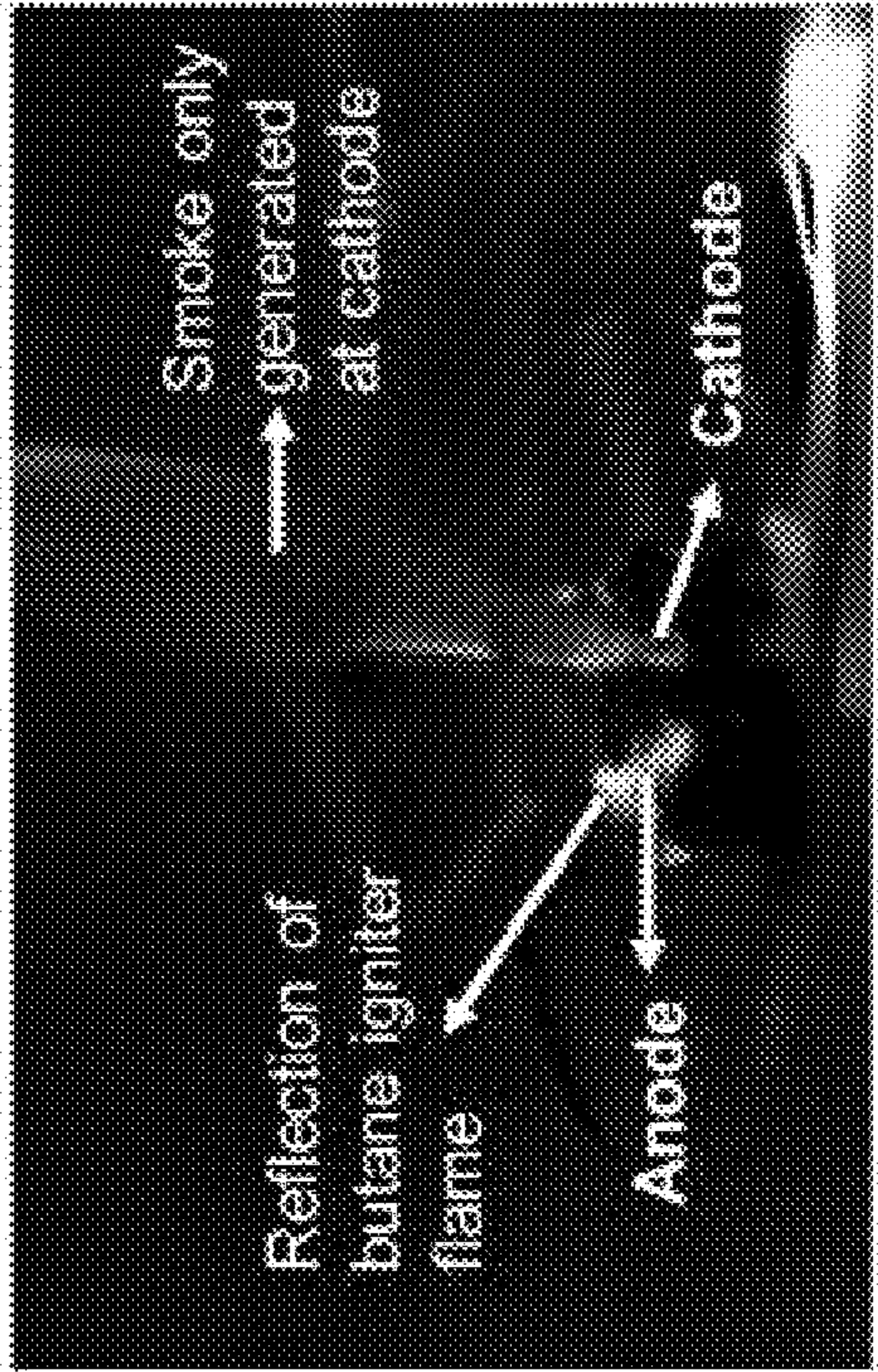


FIG. 9A

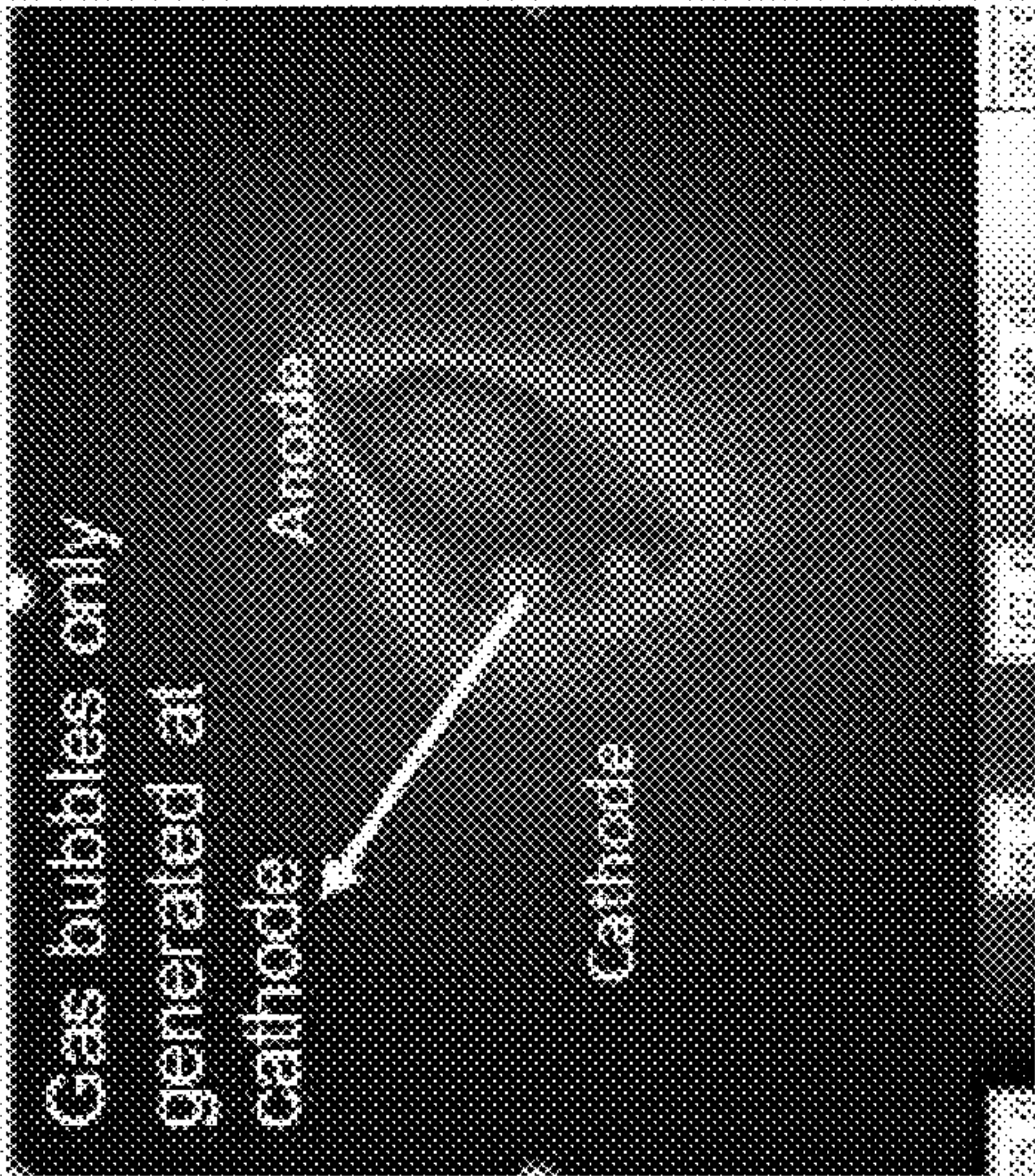


FIG. 9B

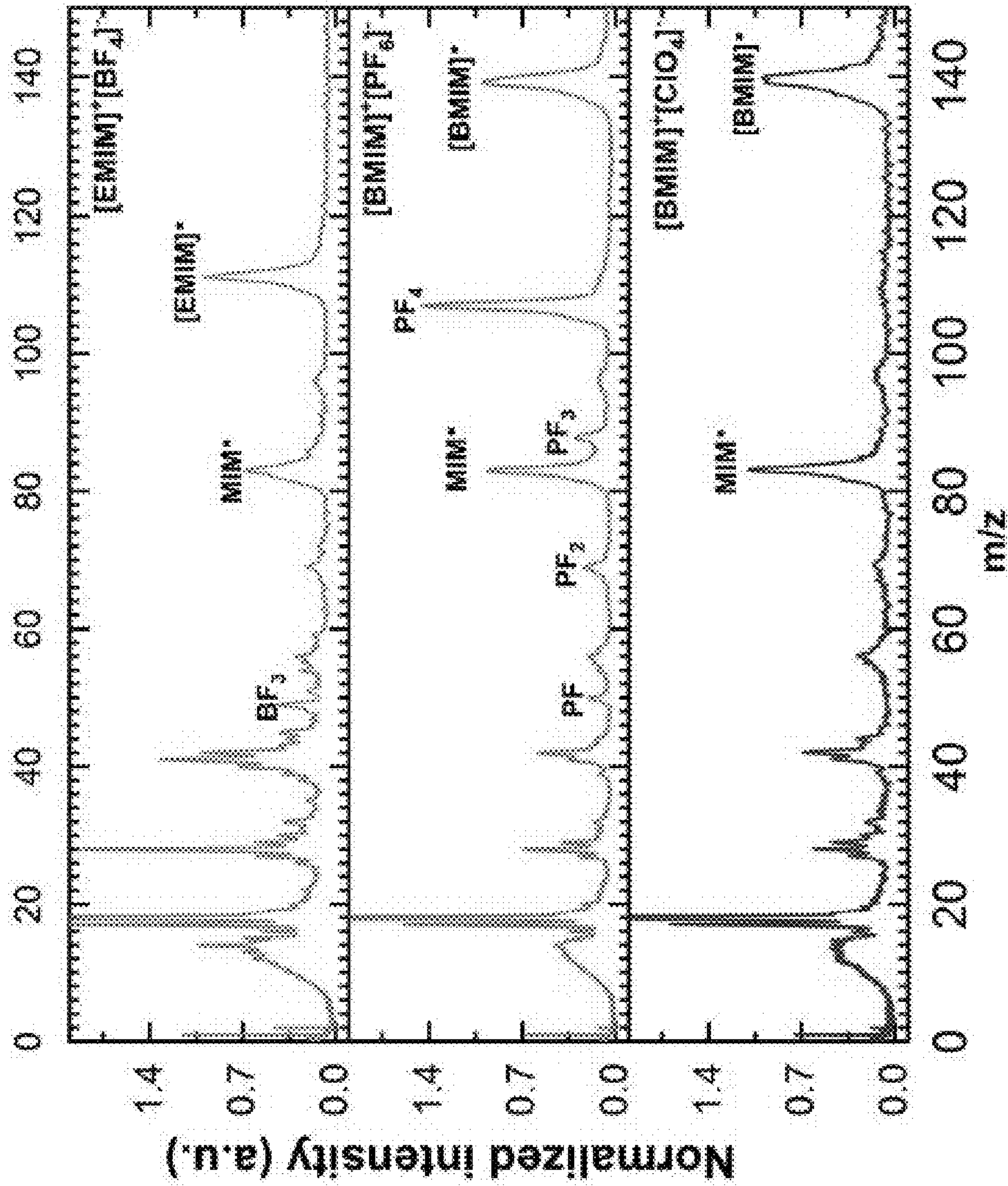


FIG. 10

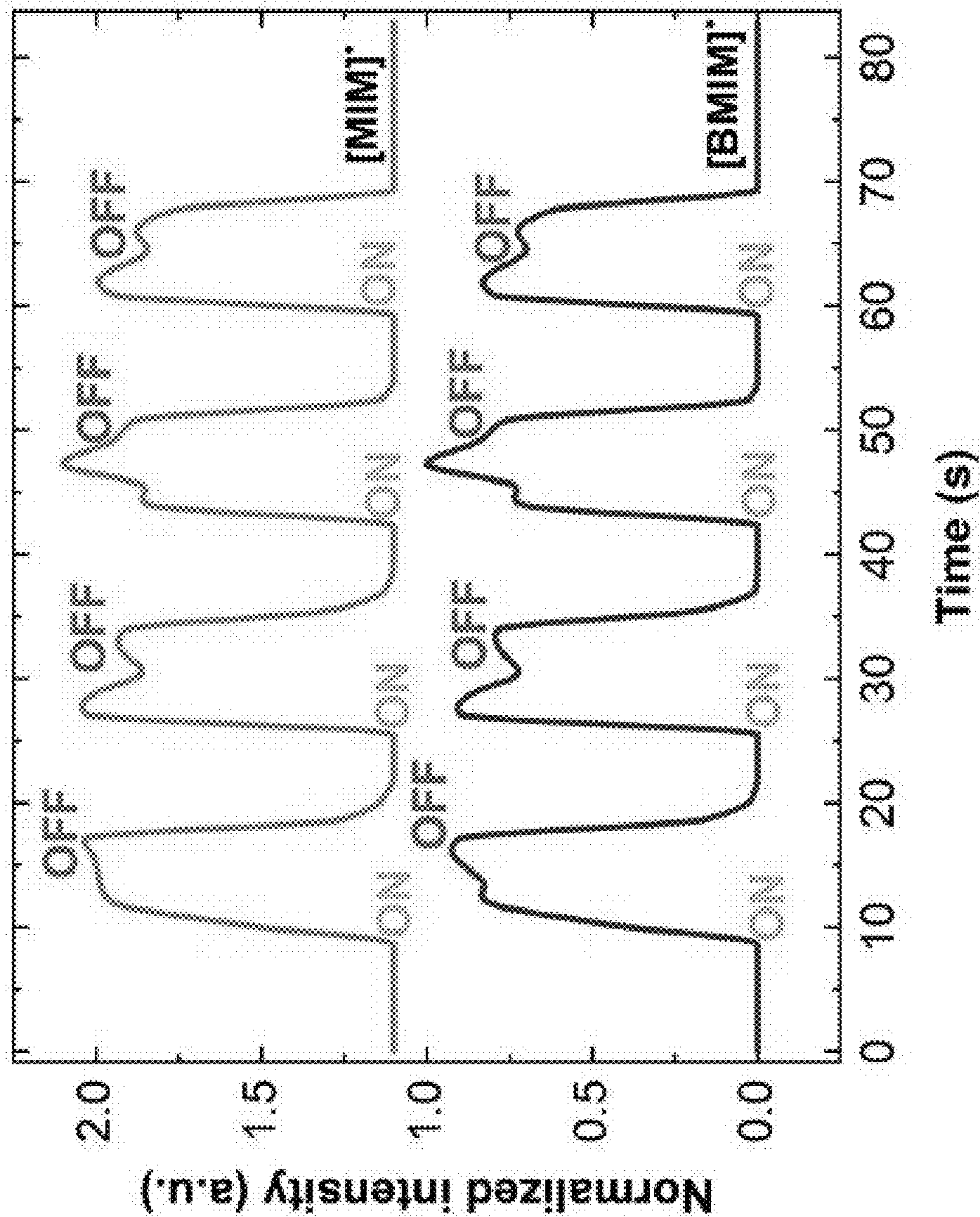


FIG. 11

1200

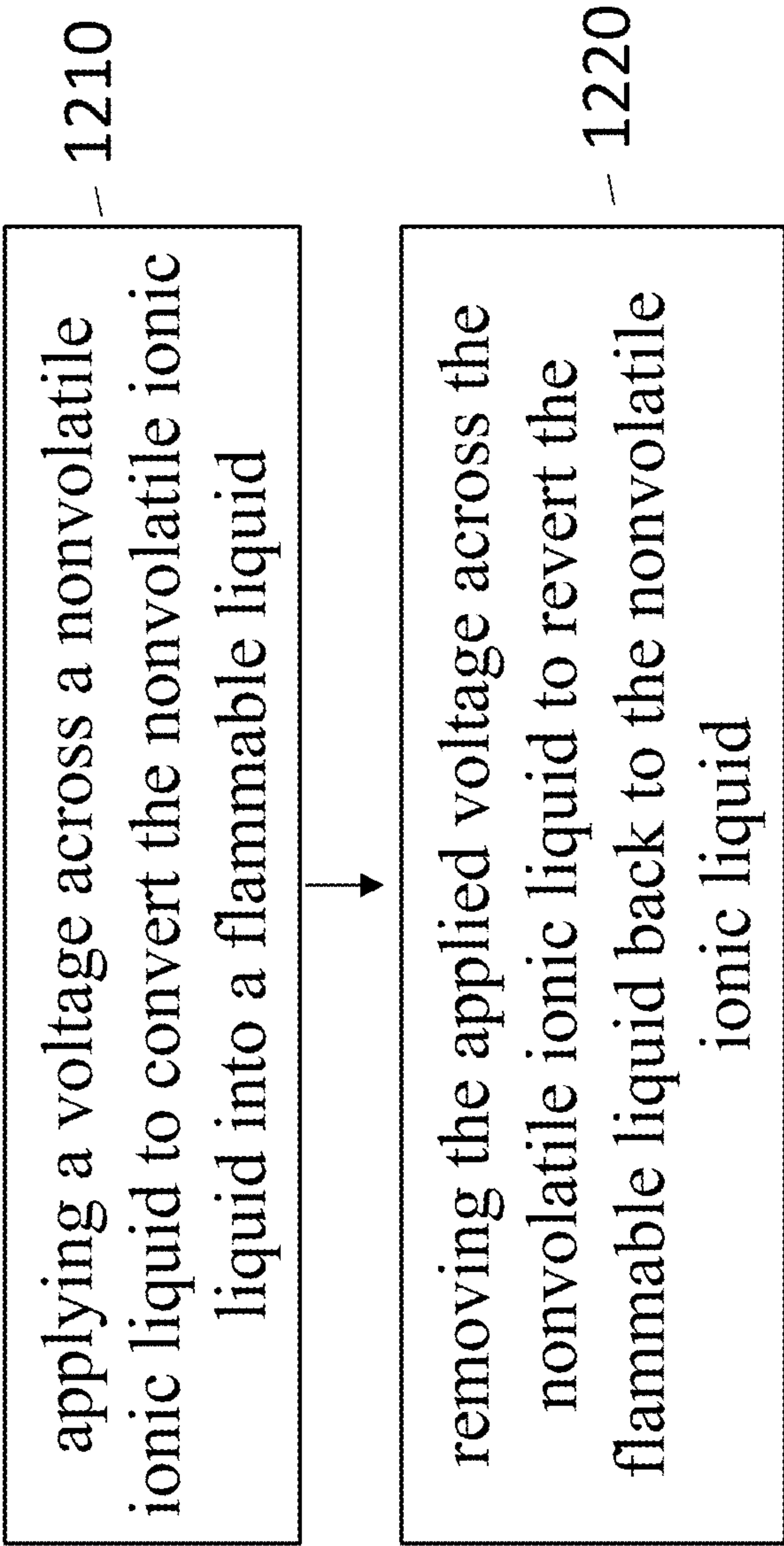


FIG. 12

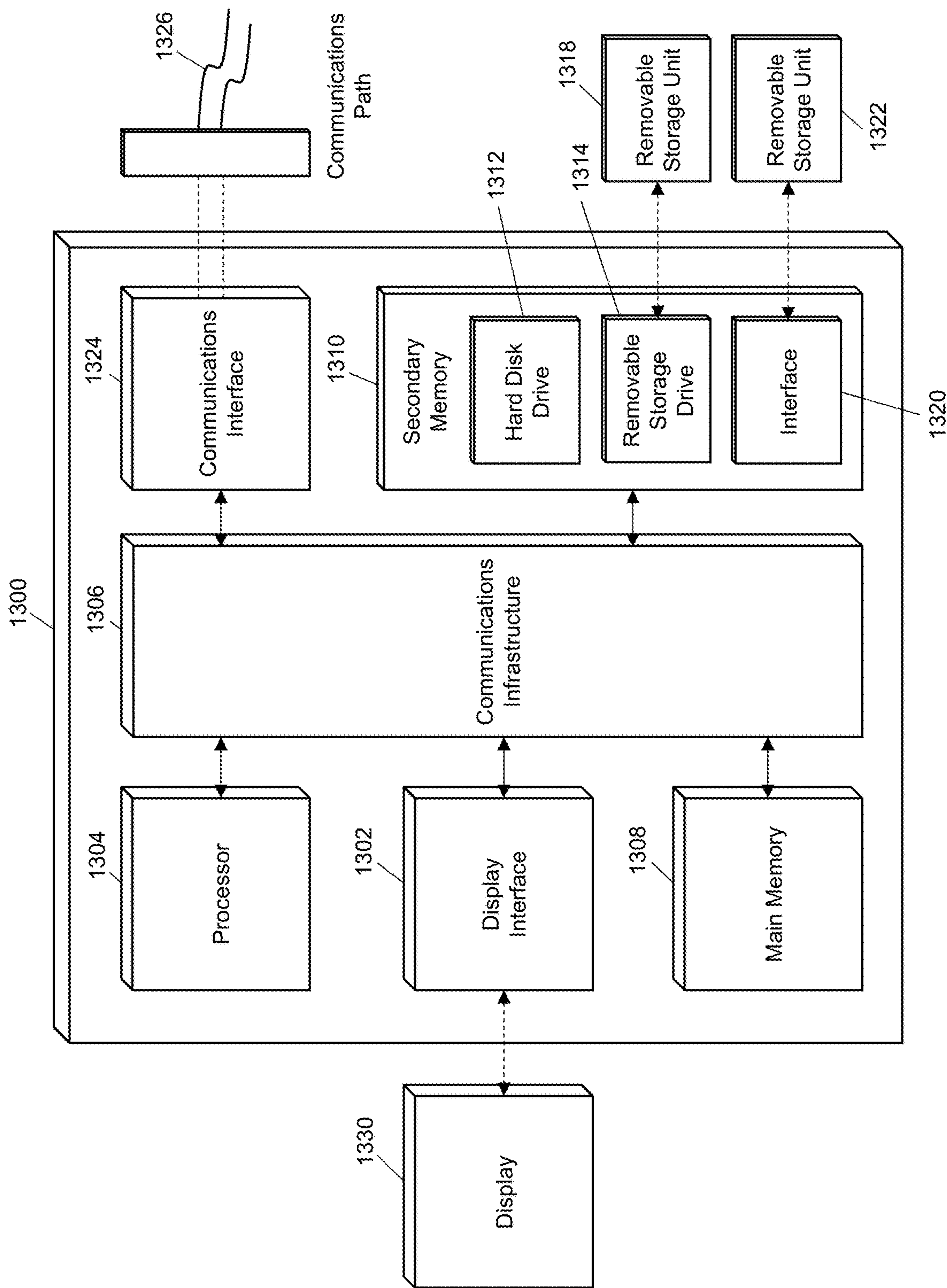


FIG. 13

ELECTROCHEMICAL MODULATION OF THE FLAMMABILITY OF IONIC LIQUID FUELS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application 63/485,061, filed Feb. 15, 2023, which is incorporated by reference in its entirety.

STATEMENT OF FEDERALLY SPONSORED RESEARCH

[0002] This invention was made with Government support under contract number N00014-21-1-2038 from the Office of Naval Research (ONR). The Government has certain rights in the invention.

TECHNICAL FIELD

[0003] The present disclosure relates generally electrochemical modulation of the flammability of ionic liquid fuels.

BACKGROUND

[0004] Storage and transportation of all conventionally used high energy density fuels have the potential to cause unintended fire and explosion. Liquid hydrocarbons which are typically used as fuels combust in the vapor phase, and the heat feedback from the flame is able to vaporize enough fuel to self-sustain the combustion. Therefore, the typical way to extinguish a flame is to remove the oxygen source (air) from the flame front. Alternatively, room temperature ionic liquids (RTIL) are a special class of hydrocarbons having extremely low vapor pressures, which on thermal decomposition produces oxidation resistant species. Owing to these characteristics, RTILs are usually nonflammable and are often used as flame-retardant components in various materials for energy storage and conversion.

[0005] However, RTILs also possess high energy densities which make them attractive fuel candidates for propulsion. Energetic ionic liquids consisting of metastable anions such as azide, dinitramide, borohydride, and azole-based anions are known to thermally decompose to reactive flammable species. This has led to the use of such RTILs as fuel components in propellant and explosive formulations. Additionally, thermally insensitive RTILs which are devoid of such reactive anions can also be chemically activated with white fuming nitric acid. When brought in contact with the acid, the RTILs are spontaneously oxidized, resulting in hypergolic ignition. Termination of such a combustion process is difficult as it requires the segregation of the fuel and oxidizer.

SUMMARY

[0006] In accordance with an embodiment, by dynamically manipulating the volatility of a nominally volatile and thermally stable RTIL, it is possible to (a) store an involatile energetic liquid as nonflammable fuel, (b) make the involatile energetic liquid flammable by increasing its volatility, and (c) extinguish its flame by decreasing its volatility. The realization of this approach will offer the potential to make a “safe fuel” or alternatively lay the foundation of a simple

fuel metering scheme, which has never been realized before in the domain of condensed phase propellants.

[0007] In accordance with another embodiment, a method for controlling flammability of a fuel, the method comprising: applying a voltage across a nonvolatile ionic liquid to convert the nonvolatile ionic liquid into a flammable liquid; and removing the applied voltage across the nonvolatile ionic liquid to revert the flammable liquid back to the nonvolatile ionic liquid.

[0008] In accordance with a further embodiment, a system for controlling flammability of a fuel, the system comprising: a nonvolatile ionic liquid; a power supply configured to supply a voltage across the nonvolatile ionic liquid; and a processor configured to control the voltage across the nonvolatile ionic liquid to convert the nonvolatile ionic liquid into a flammable liquid by applying the voltage across the nonvolatile liquid and to revert the flammable liquid back to the nonvolatile ionic liquid by removing the applied voltage across the nonvolatile ionic liquid.

[0009] In accordance with an embodiment, a non-transitory computer-readable medium (CRM) storing computer program code executed by a computer processor that performs a process for controlling flammability of a fuel, the processing comprising: applying a voltage across a nonvolatile ionic liquid to convert the nonvolatile ionic liquid into a flammable liquid; and removing the voltage across the nonvolatile ionic liquid to revert the flammable liquid back to the nonvolatile ionic liquid.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] FIG. 1 is an illustration of a concept of switching the flammability of RTILs via electrolysis. Imidazolium based RTILs are inherently insensitive to thermal shock/spark; however, they can be electrochemically volatilized to reactive flammable species, which can ignite and self-sustain a flame. Turning off the voltage terminates volatilization of the RTIL, thereby extinguishing the flame. This process can be repeated several times to sequentially meter the energy from the RTIL.

[0011] FIG. 2A is an illustration of High-speed camera imaging of the electrochemical activation and deactivation of the combustion process of RTIL demonstrating the concept presented in FIG. 1, and FIG. 2B is an illustration of flame area as a function of time from the high-speed camera imaging.

[0012] FIG. 3A is a time-averaged electrochemical TOFMS spectra of [BMIM][ClO₄]-showing the evolution of volatile species from the RTIL, FIG. 3B is an illustration of an electrochemical reduction mechanism of [BMIM]⁺ to gas phase [BMIM]· and [MIM]·, and FIG. 3C illustrates a sequential volatilization of [BMIM][ClO₄]⁻ as inflammable [BMIM]·.

[0013] FIG. 4 is a chart illustrating that the peak around 1070 cm⁻¹ can be attributed to the Cl=O groups, which indicates that the synthesized ionic liquid is [BMIM][ClO₄]⁻ as it has Cl=O bonds in its anion.

[0014] FIG. 5 is a chart illustrating X-ray crystallography (XRD) of the solid precipitate formed after the hard acid soft base reaction between dissolved [BMIM][Cl]⁻ and NaClO₄ for (BMIM)[ClO₄]⁻ synthesis: [BM/M][Cl]⁻ + NaClO₄ = [BMIM][ClO₄]⁻ + NaCl(s). The XRD peaks of the solid residue matches with the peaks for the standard reference peaks for NaCl, which confirms that the hard acid soft

base reaction have occurred successfully and [BMIM]⁺[ClO₄]⁻ in the liquid phase after separation of the solid residue has been obtained.

[0015] FIG. 6 is a chart illustrating of TAG Mass loss versus Temperature for [BMIM]⁺[ClO₄]⁻ that shows 80% mass loss between 250-350° C. and the decomposition reaction is exothermic. No other endothermic peaks are observed prior to the decomposition temperature confining indicating negligible vaporization of the RTIL on heating.

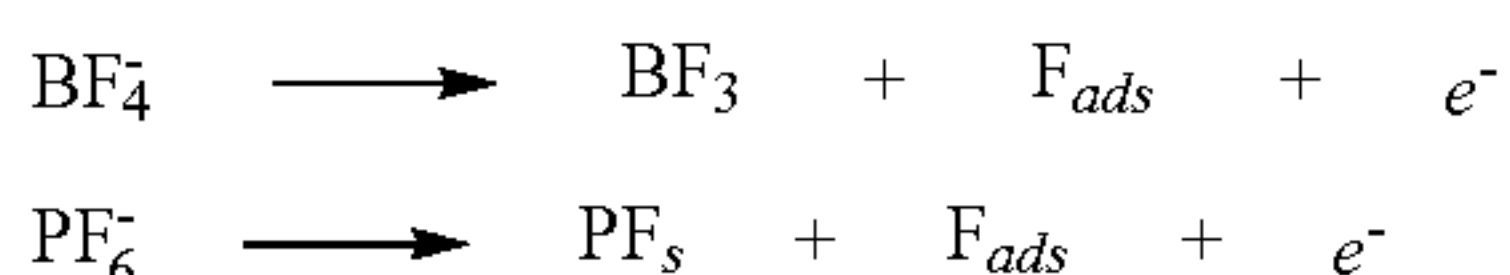
[0016] FIG. 7 is a film of the viscous RTIL ([BMIM]⁺[ClO₄]⁻), coated on wire and heated at approximately 105 K/s, shows mild flashes/gas generation. No self-sustained flame is observed, which implies that the RTIL is non-flammable.

[0017] FIG. 8 are images of an aliquot of the RTIL placed on a glass slide cannot be ignited by a butane flame, which indicates that the RTIL is thermally insensitive and non-flammable.

[0018] FIG. 9A is a high-speed optical camera image showing that smoke is only generated at the cathode when the DC bias is applied. The smoke is due to the condensation of the vapor phase species generated on electrolysis at the cathode possibly by the mechanism presented in FIG. 3B.

[0019] FIG. 9B is a high speed IR-camera imaging of the electrolysis process when the DC bias is applied. The gas bubbles are only generated at the cathode and there are insignificant number of gas bubbles near the anode, which again confirms the mechanism in FIG. 3B, where the cation [BMIM]⁺ is reduced to gas phase species at the cathode, and the oxidized products of the anion ClO₄⁻ is retained in the condensed phase.

[0020] FIG. 10 is an illustration of BMIM and EMIM cations form BMIM and EMIM radicals and butene following the mechanism suggested in FIG. 3B, which suggests that the reaction mechanism of the cation is independent of the chain length of the alkyl tail (butyl/ethyl) attached to the ring. No peaks from the anion is observed in case of [BMIM]⁺[ClO₄]⁻. [BMIM]⁺[PF₆]⁻ shows all the characteristic peaks of PF₅ gas (ionization mass spectra data from NIST webbook). [EMIM]⁺[BF₄]⁻ also shows all the characteristic peaks of BF₃. Hence, the oxidation mechanism at the anode for these two cases can be explained by the following equations:



Since, the ClO₄⁻ do not show any gas phase species, its oxidized products are probably retained in the condensed phase as explained in FIG. 3B.

[0021] FIG. 11 is an illustration of the MIM radical following the same temporal trend as the BMIM radical when the applied DC bias is turned on/off, which implies that these volatile species can be generated at the same time by applying the DC bias and an open circuit stops their generation with similar delay times.

[0022] FIG. 12 is a flow chart illustrating a method for controlling flammability of a fuel in accordance with an embodiment.

[0023] FIG. 13 illustrates a representative computer system in which embodiments of the present disclosure, or portions thereof, may be implemented as computer-readable code executed on hardware.

DETAILED DESCRIPTION

[0024] Set forth below with reference to the accompanying drawings is a detailed description of embodiments of electrochemical modulation of the flammability of ionic liquid fuels. Note that since embodiments described below are preferred specific examples of the present disclosure, although various technically preferable limitations are given, the scope of the present disclosure is not limited to the embodiments unless otherwise specified in the following descriptions.

[0025] Flammability and combustion of high energy density liquid propellants are controlled by their volatility. In accordance with an exemplary embodiment, a new concept is demonstrated in which the volatility of a high energy density ionic liquid propellant can be dynamically manipulated enabling one to (a) store a thermally insensitive oxidation resistant nonflammable fuel, (b) generate flammable vapor phase species electrochemically by applying a direct-current voltage bias, and (c) extinguish the flame of the ionic liquid propellant by removing the voltage bias, which stops the volatilization of the ionic liquid propellant. In accordance with an embodiment, a thermally stable imidazolium-based energy dense ionic liquid is disclosed that can be made flammable or nonflammable by application or withdrawal of a direct-current bias. This cycle can be repeated as often as desired. The estimated energy penalty of the electrochemical activation process is only of the total energy release. This approach presents a paradigm shift, offering the potential to make a “safe fuel” or alternatively a simple electrochemically driven fuel metering scheme.

[0026] Herein, the aromaticity of the imidazole ring, which makes the imidazolium based RTILs thermally stable and oxidation resistant, can be broken electrochemically, resulting in the volatilization of the RTIL as flammable reactive species, which can ignite and generate a self-sustaining flame. Additionally, the removal of the applied voltage bias terminates the electrochemical reactions, thereby stopping the volatilization of the RTIL resulting in the extinction of the flame. This facile strategy can be employed to control the energy generation from high energy density propellants. Such control on the energy release from condensed phase propellants, enabling on-demand extinction of the flame, has not been demonstrated previously.

[0027] A system 100 illustrating the concept of flammability switching is illustrated in FIG. 1. As shown in FIG. 1, the system 100 includes a source of a nonvolatile ionic liquid 110. In accordance with an embodiment, a voltage is applied or introduced across a nonvolatile ionic liquid (i.e., voltage ON) to convert the nonvolatile ionic liquid into a flammable liquid 120. The voltage converts the nonvolatile ionic liquid via electrolysis to vaporize at least a portion of the nonvolatile ionic liquid. In accordance with an exemplary embodiment, the vaporized nonvolatile liquid becomes a flammable liquid that can spontaneously ignite and combust (i.e., can ignite and self-sustain a flame). The applied voltage can be removed (i.e., voltage OFF) from across the nonvolatile ionic liquid to revert the flammable liquid back to the nonvolatile ionic liquid 140. The removal of the applied

voltage results in a complete flame of the nonvolatile ionic liquid **150**. The process for flammability switching can be repeated as desired **160**.

[0028] As set forth, nonflammable imidazolium RTILs are resistant to thermal shock and oxidation. However, when a voltage is applied across the RTIL, electrolysis of the RTIL results in its volatilization into flammable gas phase species, which can spontaneously ignite and combust. Continuous application of the voltage ensures continuous supply of reactive volatile fuel fragments to the flame, thereby leading to self-sustaining combustion. Withdrawing the voltage stops the volatilization of the RTIL, terminating the supply of the flammable species from the liquid phase to the flame, thereby leading to the extinction of the flame. As the RTIL is thermally insensitive, the heat feedback from the flame is not able to generate significant vapor pressure or flammable gas phase species from the fuel. Hence, it can only ignite the flammable vapor phase species generated electrochemically and is unable to ignite the liquid RTIL. Leveraging this property, the vaporization and hence the flammability of the RTIL can be completely switched off by deactivating the electrochemical reactions through withdrawal of the voltage. Hence, the flammability of the RTIL can be completely reversed at will, by electrochemical means.

[0029] In accordance with an embodiment, 1-butyl 3-methyl imidazolium perchlorate ($[\text{BMIM}]^+[\text{ClO}_4]^-$) can be synthesized by a hard acid soft base anion exchange method by reacting dissolved precursors $[\text{BMIM}]^+[\text{Cl}]^-$ and NaClO_4 as shown in FIGS. 4 and 5. Prior studies have reported that, on thermal decomposition, the imidazolium ion forms 1-methylimidazole in the vapor phase and imidazole oligomers in the liquid phase. Therefore, the oxidation resistant aromatic imidazole ring remains intact in both phases, which makes the RTIL nonflammable. Thermogravimetric analysis coupled with differential scanning calorimetry (TGA/DSC) measurements show that $[\text{BMIM}]^+[\text{ClO}_4]^-$ exothermically loses 80% of its mass between approximately 523 K and 610 K (FIG. 6), which can be attributed to the generation of vapor phase imidazoles. Although this RTIL undergoes exothermic thermal decomposition, it has been demonstrated that the RTIL cannot be ignited thermally by hot-wire ignition at high heating rates (FIG. 7) or by contacting a butane flame (FIG. 8), thereby proving that the RTIL is resistant to thermochemically driven oxidation.

[0030] However, the combustion event of $[\text{BMIM}]^+[\text{ClO}_4]^-$ can be electrochemically activated/deactivated in multiple cycles, as demonstrated in FIG. 2. For example, $[\text{BMIM}]^+[\text{ClO}_4]^-$ liquid can be electrochemically activated with two Pt-wire electrodes ($\sim 75 \mu\text{m}$ diameter), as shown in the representative schematic (FIG. 1). When the voltage ($V=40 \text{ V}$) is applied, in the absence of an external igniter, smoke and gas bubbles are generated only at the cathode as observed by high-speed optical and IR imaging (FIG. 9). FIG. 2A illustrates that when a butane flame is held above the surface of the RTIL after turning on the voltage, the gaseous species released can be ignited. The flame height gradually grows and becomes constant indicating the ability of the gaseous species generated on electrolysis to undergo self-sustaining combustion. When the voltage is turned off, the flame height decreases, and the flame is extinguished as the generation and supply of volatile flammable species to the flame is inhibited. The flame area from these images have been estimated by counting the number of bright pixels

after excluding the frames containing the butane flame, and the time-evolution of the normalized flame area has been represented in FIG. 2B after moving average smoothing, to corroborate the visual observations presented in FIG. 2A, which clearly demonstrates the aforementioned concept of controlling the thermal energy generation from RTILs, by sequentially dispensing and combusting volatile species from the condensed phase RTIL, which remains unaffected by the heat feedback from the flame.

[0031] In accordance with an embodiment, a voltage of 40 volts (V) was used for the demonstration purpose. However, considering the electrochemical stability window of the RTILs from voltametric measurements, any applied voltage above approximately 6 volts (V) to 40 volts (V) will be able to electrolyze the given RTIL.

[0032] The model RTIL, $[\text{BMIM}]^+[\text{ClO}_4]^-$, has been electrolyzed under vacuum, and the evolving vapor and gas phase species have been directly sampled and analyzed by time-of-flight mass spectrometry as explained in the methods section described below. The time-averaged mass spectra (FIG. 3A) collected over approximately 100 ms by sampling at an interval of approximately 0.1 ms shows the generation of 1-methyl 3-butyl imidazole-2-yl radical ($[\text{BMIM}]^*$, $m/z=139$), 1-methyl imidazole-2-yl radical ($[\text{MIM}]^*$, $m/z=83$), and butene ($m/z=28, 41, 56$).

[0033] The generation of these radicals can be explained by the cathodic reduction of the BMIM cation, as shown in FIG. 3B. On gaining an electron, the isomer of the BMIM cation having a methyl group attached to the N^+ forms $[\text{BMIM}]^*$ whereas the other isomer with the butyl group attached to the N^+ results in the formation of $[\text{MIM}]^*$ and butene. In order to verify this mechanism, we also characterized other commercially available RTILs such as $[\text{BMIM}]^+[\text{PF}_6]^-$ and $[\text{EMIM}]^+[\text{BF}_4]^-$. The $[\text{BMIM}]^+[\text{PF}_6]^-$ shows both $[\text{BMIM}]^*$ and $[\text{MIM}]^*$ peaks (FIG. 10), as observed in the case of $[\text{BMIM}]^+[\text{ClO}_4]^-$, indicating that the cathodic reaction of the BMIM-cation is independent of the anion attached to it. The $[\text{EMIM}]^+[\text{BF}_4]^-$ also shows $[\text{EMIM}]^*$ and $[\text{MIM}]^*$ peaks (FIG. 10), indicating that the formation of imidazole-2-yl radicals by cathodic reduction is independent of the alkyl chain length attached to the N^+ of the BMIM-cation, which shows that the electrochemical reduction mechanism shown in FIG. 3B can be generically applied to all imidazolium-based cations. The existence and the stability of these radicals have been also reported in previous studies. The absence of vapor phase species from the anodic reaction indicates the $[\text{ClO}_4]^-$ has undergone partial oxidation to chlorate ($[\text{ClO}_3]^-$) and chlorite ($[\text{ClO}_2]^-$) ions, as its complete transformation to gas phase chlorine and oxygen requires multiple electron transfers, which is highly unlikely in the absence of an electro-catalyst. This is also supported by the fact that BF_3 and PF_5 gases appear in the obtained mass spectra of $[\text{EMIM}]^+[\text{BF}_4]^-$ and $[\text{BMIM}]^+[\text{PF}_6]^-$ respectively (FIG. 10), from one-electron oxidation of the respective anions.

[0034] Thus, electrochemical reduction breaks the aromaticity of the imidazole ring, thereby generating gas phase $[\text{BMIM}]^*$, $[\text{MIM}]^*$, and butene. As the aromaticity of the imidazole ring significantly limits the flammability of the RTIL, its absence makes the generated gas phase species prone to oxidation and hence these evolved species are highly flammable. Additionally, as shown in FIG. 3C, it is possible to sequentially dispense $[\text{BMIM}]^*$ by turning on/off the external voltage periodically. The volatility of $[\text{MIM}]^*$

(FIG. 11) can also be manipulated in the same manner as that of [BMIM]⁺ by periodically controlling the external voltage. This corroborates the temporal variation of the flame area on application and withdrawal of the direct-current bias (FIG. 2). This indicates that the application of the direct-current bias on the RTIL generates volatile flammable species such as [BMIM]⁺, [MIM]⁺, and butene leading to a self-sustained flame, whereas an open circuit stops the volatilization of the RTIL into these species, thereby extinguishing the flame.

[0035] In summary, it has been demonstrated for the first time that the flammability of a thermally insensitive, oxidation resistant liquid fuel can be reversed by applying and withdrawing a voltage across it. Therefore, this approach does not require any separation of fuel from the oxidizer to manipulate flammability. In the current study, this effect has been demonstrated by using a nonflammable model imidazolium based room temperature ionic liquid (RTIL). The aromaticity of the imidazole ring makes the RTIL resistant to thermal shock and oxidation. The aromaticity can be broken by electrochemical reduction of the imidazolium ion, which results in its gasification, and the evolved gases being more prone to oxidation can be ignited and combusted. Removal of the voltage shuts off the electrochemical reduction process, thereby cutting off the supply of volatile flammable species to the flame, resulting in its complete extinction.

[0036] In accordance with an embodiment, the complete combustion of imidazolium ionic liquids can potentially generate approximately 20 KJ/g according to the calculations, whereas the work performed to electrolyze the liquid is approximately 0.8 KJ/g; that is, the energy penalty associated with the electrolysis process is only 4%. Thus, these findings may bring in a paradigm shift by enabling the use of RTILs as safe energy-dense fuels, the energy generation from which can be controlled in a sequential manner. Moreover, this disclosure lays the foundation of several fundamental studies that will focus on evaluation of the major degrees of freedom controlling the thermal energy release profile of these systems along with the characterization of their flame temperature and energy release rates.

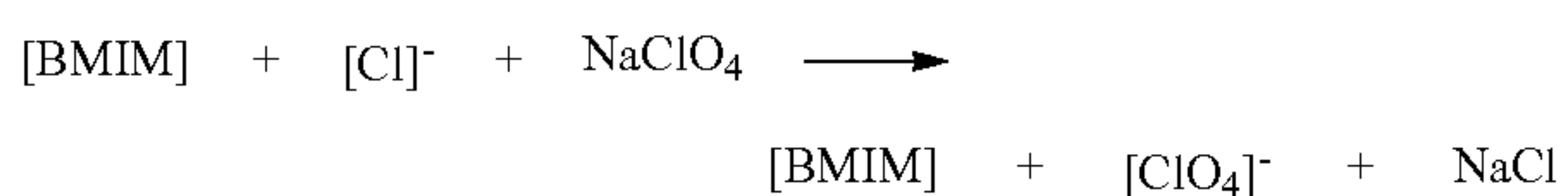
Methods

Chemicals

[0037] [BMIM]⁺[Cl]⁻ (~98%) solid powder (m.p. approximately 70° C.) were procured from Sigma Aldrich. NaClO₄ crystals and solvents such as ethanol and acetonitrile were obtained from Fischer scientific.

Synthesis of [BMIM]⁺[ClO₄]⁻

[0038] [BMIM]⁺[ClO₄]⁻ was synthesized by a hard acid soft base anion exchange reaction between [BMIM]⁺[Cl]⁻ with NaClO₄:



4 ml of a 1.4 M solution of [BMIM]⁺[Cl]⁻ in ethanol was added to 6 ml 0.96 M solution of NaClO₄ in ethanol to perform the above reaction. The resulting white precipitate of NaCl was centrifuged and separated. The liquid obtained after separation of the NaCl, was washed with acetonitrile as

an antisolvent to precipitate trace amounts of dissolved NaCl. The white precipitate of NaCl was centrifuged and separated again. The liquid obtained after washing was dried in vacuum oven overnight to evaporate the ethanol and obtain [BMIM]⁺[ClO₄]⁻ as a room temperature ionic liquid. The solid residue of NaCl as a product of the reaction is removed by centrifugation and the ethanol is removed from the supernatant by vacuum drying to obtain [BMIM]⁺[ClO₄]⁻. ATR-FTIR spectra (FIG. 4) confirms the presence of the ClO₄ groups in the synthesized [BMIM]⁺[ClO₄]⁻. XRD of the solid white residue shows that it is NaCl (FIG. 5), thereby confirming the hard acid soft base ion exchange reaction has occurred successfully, resulting in the formation of [BMIM]⁺[ClO₄]⁻.

Characterizations of the RTIL

[0039] ATR-FTIR characterizations have been performed using ThermoFisher Nicolet iS50R, for compositional analysis. X-ray Diffraction has been performed using PANalytical EMPYREAN (Cu Kα source, λ=1.54 Å) to identify the composition of the solid residue during the RTIL synthesis. Thermo-gravimetric analysis (TGA) was performed using Netzsch STA 449 F3.

Experiments for Demonstrating on/Off Switching of Flammability

[0040] For performing the combustion experiments under electrochemical stimulation, aliquots of the ionic liquid was placed in the center of the watch glass. Two Pt wire electrodes having a diameter of approximately 75 μm were immersed into the ionic liquids. The Pt wires were directly connected through copper alligator clips to the +ve and -ve terminals of a DC power supply. A DC bias of approximately 40 volts (V) was applied to electrolyze the ionic liquid. Then a butane flame generated by a commercial lighter was held above the surface of the RTIL placed on the watch glass, to ignite the volatile species released from the RTIL on electrolysis. After ignition of the gas phase species, the butane lighter was retracted from the surface of the RTIL, to allow the volatile species which are constantly generated under the DC bias, to self-sustain a flame. Once the flame was self-sustained, the DC bias was removed to create an open circuit to stop the generation of the volatile species and extinguish the flame. This process was repeated in several cycles. The high speed imaging was performed using a Phantom Miro 110 camera.

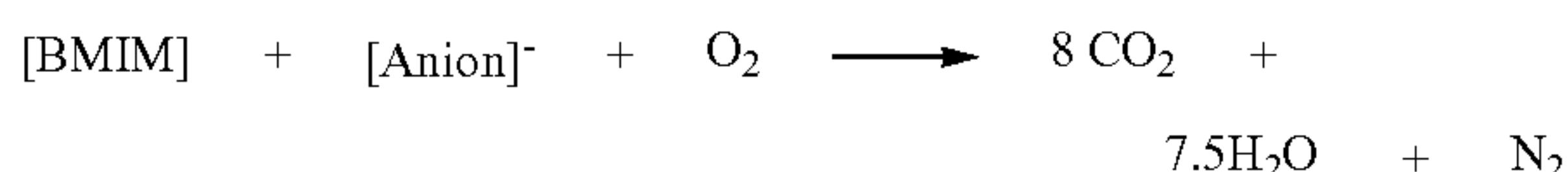
Electrochemical Time of Flight Mass Spectrometry of the RTIL for In-Situ Identification of the Volatile Species Generated on its Electrolysis

[0041] An assembly of aliquots of the RTIL placed on a glass slide with the approximately 75 μm diameter Pt wire electrodes immersed in it, connected to the terminals of the same DC power supply as described in the previous section, were inserted into the high vacuum (approximately 10⁻⁹ atm) chamber of a time-of-flight mass spectrometer. The assembly was inserted right in between the ion extractor plates of the time-of-flight assembly. The gas phase species generated on electrolysis where ionized by an approximately 70 eV electron gun and the positive ions were extracted and accelerated through the time-of-flight tube to be detected by the time-of-flight method. A parabolic calibration curve (m/z=at²+bt+c) generated from a combination of standard samples such as SF₆ gas and vaporization/thermal decom-

position of solid Bi_2O_3 , CuO and I_2O_5 was used to identify the m/z values from the time-of-flight. For obtaining the average spectra, the DC bias was applied to the ionic liquid through the Pt electrodes. The volatile species generated was ionized and the positive ions were sampled and detected for 100 ms at every 0.1 ms by pulsing the voltage across the extractor plates. For demonstrating that the generation of the volatile species can be switched on/off through the DC bias, the mass spectra was obtained at every approximately 1.7 s intervals over a period of seconds. The data acquisition was performed with high frequency Teledyne Lecroy oscilloscope and the data analysis was performed through custom built MATLAB scripts. More details about the working principle of the time-of-flight component of this characterization can be found elsewhere.

Calculation on Enthalpy of Combustion and Electrochemical Work Performed

[0042]



[0043] The enthalpy of formation of both gas and liquid $[\text{BMIM}]^+[\text{DCA}]^-$ are known. As the enthalpy of combustion majorly depends on the bulky fuel cation, it can be assumed that the combustion enthalpy of BMIM based ionic liquids will be roughly similar.

[0044] $\Delta H_{\text{gas}} = 363.4 \text{ KJ/mol}$; $\Delta H_{\text{liquid}} = 206.2 \text{ KJ/mol}$; $\Delta H_{\text{CO}} = -393.5 \text{ kJ/mol}$ (NIST); $\Delta H_{\text{H}_2\text{O}} = -241 \text{ kJ/mol}$ (NIST)

[0045] From this, the combustion enthalpy of gas phase BMIM ionic liquid is -4592 KJ/mol and that of liquid phase is -4749 KJ/mol . However, on gravimetric basis both are approximately same approximately 20 KJ/g .

[0046] Cyclic voltammetry measurement on $[\text{BMIM}]^+[\text{ClO}_4]^-$ have reported that the cathodic reaction $[\text{BMIM}]^+$ to BMIM radical occurs between -1.4 V to 2 V , which is basically the work required to make the free energy of the system to be negative to obtain a spontaneous reaction. Hence, the electrochemical work required is Faraday constant times the voltage $\sim 193 \text{ KJ/mol}$ which is ~ 0.81 on a gravimetric basis.

[0047] As set forth, the ability to control combustion underpins many processes occurring on a daily basis, including the injection of fuel into internal combustion engines or adding wood to a fire. However, owing to their high energy density, storage and transport of fuels can be fraught with danger if not handled properly, hence the stringent safety measures for fuel trucks and tankers.

[0048] In accordance with an exemplary embodiment, the volatility of an energy-dense room-temperature ionic liquid, for example, 1-butyl 3-methyl imidazolium perchlorate ($[\text{BMIM}]^+[\text{ClO}_4]^-$), can be controlled through electrochemistry. On its own, this ionic liquid is thermally stable and resistant to oxidation, even in contact with a flame, the liquid will not ignite. This stability is due to the aromaticity of the imidazole. However, applying a voltage to the ionic liquid breaks this aromaticity, and $[\text{BMIM}]$ and $[\text{MIM}]$ radicals form through cathodic reduction, as well as butene, which

are released into the gas phase. These gas-phase species are more prone to oxidation, are volatile and readily set alight.

[0049] Once electrochemically activated and ignited, the combustion process continues until the power is switched off, whereafter the aromaticity of the imidazolium ion is restored. As the aromaticity can be broken and restored at will, this process can be cycled as often as desired as long as the 'fuel' is present.

[0050] Simply heating the imidazolium ion, without breaking the aromaticity, leads to the ionic liquid decomposing to 1-methylimidazole in the vapour phase and imidazole oligomers in the liquid phase. Both of these products retain their aromaticity and are therefore thermally stable, hence the essential need of electrochemistry and why the fire is extinguished when the power is switched off. The team also tested other commercially available aromatic ionic liquids, which also led to the electrochemically induced destruction of the aromatic ring, cathodic reduction and production of gas-phase radicals and alkenes.

[0051] According to an exemplary embodiment, about 20 KJ/g of energy can be generated from the complete combustion of $[\text{BMIM}]^+[\text{ClO}_4]^-$, but only 0.8 kJ/g is required to activate the liquid electrochemically. This minor energy penalty of about 4% can paves the way for the potential use of such room-temperature ionic liquids as fuels, with the added bonus of being safe to store and transport.

[0052] FIG. 12 illustrates a method 1200 for controlling flammability of a fuel. The method 1220 includes applying a voltage across a nonvolatile ionic liquid to convert the nonvolatile ionic liquid into a flammable liquid 1210 and removing the applied voltage across the nonvolatile ionic liquid to revert the flammable liquid back to the nonvolatile ionic liquid 1220.

[0053] In accordance with an embodiment, the nonvolatile ionic liquid is a room-temperature ionic liquid. The non-volatile ionic liquid can be an imidazolium based nonvolatile ionic liquid.

[0054] In accordance with an embodiment, the nonvolatile ionic liquid produces and releases 1-methylimidazole on application of the voltage across the nonvolatile ionic liquid. In accordance with another embodiment, the nonvolatile ionic liquid produces and releases 1-ethyl-3-methyl-on application of the voltage across the nonvolatile ionic liquid. In accordance with a further embodiment, the nonvolatile ionic liquid produces and releases 1-butyl-3-methyl-on application of the voltage across the nonvolatile ionic liquid.

[0055] In accordance with an exemplary embodiment, the method can include applying at least 6 volts to the nonvolatile ionic liquid to convert the nonvolatile ionic liquid into the flammable liquid. In another embodiment, the method further includes applying 6 volts to 40 volts to the nonvolatile ionic liquid to convert the nonvolatile ionic liquid into the flammable liquid.

[0056] In addition, the use of the nonvolatile ionic liquid and methods as disclosed herein can provide for improved safety. For example, the flammable liquid can be for use as a jet fuel, propellant, or alternate fuel. For example, the propellant can be used in satellite systems to propel the satellite to a different orbit. Alternatively, the alternate fuel could be for a ship so as to help avoid on board fires.

[0057] FIG. 13 illustrates a representative computer system 1300 in which embodiments of the present disclosure, or portions thereof, may be implemented as computer-readable code executed on hardware. For example, the one

or more computer systems associated with the method and system for controlling flammability of a fuel as disclosed herein may be implemented in whole or in part by a computer system **1300** using hardware, software executed on hardware, firmware, non-transitory computer readable media having instructions stored thereon, or a combination thereof and may be implemented in one or more computer systems or other processing systems. Hardware, software executed on hardware, or any combination thereof may embody modules and components used to implement the methods and steps of the presently described method and system.

[0058] If programmable logic is used, such logic may execute on a commercially available processing platform configured by executable software code to become a specific purpose computer or a special purpose device (for example, programmable logic array, application-specific integrated circuit, etc.). A person having ordinary skill in the art may appreciate that embodiments of the disclosed subject matter can be practiced with various computer system configurations, including multi-core multiprocessor systems, mini-computers, mainframe computers, computers linked or clustered with distributed functions, as well as pervasive or miniature computers that may be embedded into virtually any device. For instance, at least one processor device and a memory may be used to implement the above described embodiments.

[0059] A processor unit or device as discussed herein may be a single processor, a plurality of processors, or combinations thereof. Processor devices may have one or more processor “cores.” The terms “computer program medium,” “non-transitory computer readable medium,” and “computer usable medium” as discussed herein are used to generally refer to tangible media such as a removable storage unit **1318**, a removable storage unit **1322**, and a hard disk installed in hard disk drive **1312**.

[0060] Various embodiments of the present disclosure are described in terms of this representative computer system **1300**. After reading this description, it will become apparent to a person skilled in the relevant art how to implement the present disclosure using other computer systems and/or computer architectures. Although operations may be described as a sequential process, some of the operations may in fact be performed in parallel, concurrently, and/or in a distributed environment, and with program code stored locally or remotely for access by single or multi-processor machines. In addition, in some embodiments the order of operations may be rearranged without departing from the spirit of the disclosed subject matter.

[0061] A processor device **1304** may be processor device specifically configured to perform the functions discussed herein. The processor device **1304** may be connected to a communications infrastructure **1306**, such as a bus, message queue, network, multi-core message-passing scheme, etc. The network may be any network suitable for performing the functions as disclosed herein and may include a local area network (“LAN”), a wide area network (“WAN”), a wireless network (e.g., “Wi-Fi”), a mobile communication network, a satellite network, the Internet, fiber optic, coaxial cable, infrared, radio frequency (“RF”), or any combination thereof. Other suitable network types and configurations will be apparent to persons having skill in the relevant art. The computer system **1300** may also include a main memory **1308** (e.g., random access memory, read-only memory, etc.),

and may also include a secondary memory **1310**. The secondary memory **1310** may include the hard disk drive **1312** and a removable storage drive **1314**, such as a floppy disk drive, a magnetic tape drive, an optical disk drive, a flash memory, etc.

[0062] The removable storage drive **1314** may read from and/or write to the removable storage unit **1318** in a well-known manner. The removable storage unit **1318** may include a removable storage media that may be read by and written to by the removable storage drive **1314**. For example, if the removable storage drive **1314** is a floppy disk drive or universal serial bus port, the removable storage unit **1318** may be a floppy disk or portable flash drive, respectively. In one embodiment, the removable storage unit **1318** may be non-transitory computer readable recording media.

[0063] In some embodiments, the secondary memory **1310** may include alternative means for allowing computer programs or other instructions to be loaded into the computer system **1300**, for example, the removable storage unit **1322** and an interface **1320**. Examples of such means may include a program cartridge and cartridge interface (e.g., as found in video game systems), a removable memory chip (e.g., EEPROM, PROM, etc.) and associated socket, and other removable storage units **1322** and interfaces **1320** as will be apparent to persons having skill in the relevant art.

[0064] Data stored in the computer system **1300** (e.g., in the main memory **1308** and/or the secondary memory **1310**) may be stored on any type of suitable computer readable media, such as optical storage (e.g., a compact disc, digital versatile disc, Blu-ray disc, etc.) or magnetic storage (e.g., a hard disk drive). The data may be configured in any type of suitable database configuration, such as a relational database, a structured query language (SQL) database, a distributed database, an object database, etc. Suitable configurations and storage types will be apparent to persons having skill in the relevant art.

[0065] The computer system **1300** may also include a communications interface **1324**. The communications interface **1324** may be configured to allow software and data to be transferred between the computer system **1300** and external devices. Exemplary communications interfaces **1324** may include a modem, a network interface (e.g., an Ethernet card), a communications port, a PCMCIA slot and card, etc. Software and data transferred via the communications interface **1324** may be in the form of signals, which may be electronic, electromagnetic, optical, or other signals as will be apparent to persons having skill in the relevant art. The signals may travel via a communications path **1326**, which may be configured to carry the signals and may be implemented using wire, cable, fiber optics, a phone line, a cellular phone link, a radio frequency link, etc.

[0066] The computer system **1300** may further include a display interface **1302**. The display interface **1302** may be configured to allow data to be transferred between the computer system **1300** and external display **1330**. Exemplary display interfaces **1302** may include high-definition multimedia interface (HDMI), digital visual interface (DVI), video graphics array (VGA), etc. The display **1330** may be any suitable type of display for displaying data transmitted via the display interface **1302** of the computer system **1300**, including a cathode ray tube (CRT) display, liquid crystal display (LCD), light-emitting diode (LED) display, capacitive touch display, thin-film transistor (TFT) display, etc. Computer program medium and computer usable medium

may refer to memories, such as the main memory **1308** and secondary memory **1310**, which may be memory semiconductors (e.g., DRAMs, etc.). These computer program products may be means for providing software to the computer system **1300**. Computer programs (e.g., computer control logic) may be stored in the main memory **1308** and/or the secondary memory **1310**. Computer programs may also be received via the communications interface **1324**. Such computer programs, when executed, may enable computer system **1300** to implement the present methods as discussed herein. In particular, the computer programs, when executed, may enable processor device **1304** to implement the methods illustrated by FIGS. 1-12, as discussed herein. Accordingly, such computer programs may represent controllers of the computer system **1300**. Where the present disclosure is implemented using software executed on hardware, the software may be stored in a computer program product and loaded into the computer system **1300** using the removable storage drive **1314**, interface **1320**, and hard disk drive **1312**, or communications interface **1324**.

[0067] The processor device **1304** may comprise one or more modules or engines configured to perform the functions of the computer system **1300**. Each of the modules or engines may be implemented using hardware and, in some instances, may also utilize software executed on hardware, such as corresponding to program code and/or programs stored in the main memory **1308** or secondary memory **1310**. In such instances, program code may be compiled by the processor device **1304** (e.g., by a compiling module or engine) prior to execution by the hardware of the computer system **1300**. For example, the program code may be source code written in a programming language that is translated into a lower level language, such as assembly language or machine code, for execution by the processor device **1304** and/or any additional hardware components of the computer system **1300**. The process of compiling may include the use of lexical analysis, preprocessing, parsing, semantic analysis, syntax-directed translation, code generation, code optimization, and any other techniques that may be suitable for translation of program code into a lower level language suitable for controlling the computer system **1300** to perform the functions disclosed herein. It will be apparent to persons having skill in the relevant art that such processes result in the computer system **1300** being a specially configured computer system **1300** uniquely programmed to perform the functions discussed above.

[0068] The detailed description above describes embodiments for electrochemical modulation of the flammability of ionic liquid fuels. The invention is not limited, however, to the precise embodiments and variations described. Various changes, modifications and equivalents may occur to one skilled in the art without departing from the spirit and scope of the invention as defined in the accompanying claims. It is expressly intended that all such changes, modifications and equivalents which fall within the scope of the claims are embraced by the claims.

What is claimed is:

1. A method for controlling flammability of a fuel, the method comprising:

applying a voltage across a nonvolatile ionic liquid to convert the nonvolatile ionic liquid into a flammable liquid; and

removing the applied voltage across the nonvolatile ionic liquid to revert the flammable liquid back to the nonvolatile ionic liquid.

2. The method according to claim 1, wherein the nonvolatile ionic liquid is a room-temperature ionic liquid.

3. The method according to claim 1, wherein the nonvolatile ionic liquid is an imidazolium based nonvolatile ionic liquid.

4. The method according to claim 1, wherein the nonvolatile ionic liquid produces and releases 1-methylimidazole on application of the voltage across the nonvolatile ionic liquid.

5. The method according to claim 1, wherein the nonvolatile ionic liquid produces and releases 1-ethyl-3-methyl- on application of the voltage across the nonvolatile ionic liquid.

6. The method according to claim 1, wherein the nonvolatile ionic liquid produces and releases 1-butyl-3-methyl- on application of the voltage across the nonvolatile ionic liquid.

7. The method according to claim 1, further comprising: applying at least 6 volts to the nonvolatile ionic liquid to convert the nonvolatile ionic liquid into the flammable liquid.

8. The method according to claim 1, further comprising: applying 6 volts to 40 volts to the nonvolatile ionic liquid to convert the nonvolatile ionic liquid into the flammable liquid.

9. The method according to claim 1, further comprising: providing the flammable liquid for use as a jet fuel, propellant, or alternate fuel.

10. A system for controlling flammability of a fuel, the system comprising:

a nonvolatile ionic liquid;

a power supply configured to supply a voltage across the nonvolatile ionic liquid; and

a processor configured to control the voltage across the nonvolatile ionic liquid to convert the nonvolatile ionic liquid into a flammable liquid by applying the voltage across the nonvolatile liquid and to revert the flammable liquid back to the nonvolatile ionic liquid by removing the applied voltage across the nonvolatile ionic liquid.

11. The system according to claim 10, wherein the nonvolatile ionic liquid is a room-temperature ionic liquid.

12. The system according to claim 10, wherein the nonvolatile ionic liquid is an imidazolium based nonvolatile ionic liquid.

13. The system according to claim 10, wherein the nonvolatile ionic liquid produces and releases one or more of 1-ethyl-3-methyl- and 1-butyl-3-methyl- on application of the voltage across the nonvolatile ionic liquid.

14. The system according to claim 10, wherein the processor is configured to applying at least 6 volts to the nonvolatile ionic liquid to convert the nonvolatile ionic liquid into the flammable liquid.

15. The system according to claim 10, wherein the processor is configured to apply 6 volts to 40 volts to the nonvolatile ionic liquid to convert the nonvolatile ionic liquid into the flammable liquid.

16. A non-transitory computer-readable medium (CRM) storing computer program code executed by a computer processor that performs a process for controlling flammability of a fuel, the processing comprising:

applying a voltage across a nonvolatile ionic liquid to convert the nonvolatile ionic liquid into a flammable liquid; and

removing the voltage across the nonvolatile ionic liquid to revert the flammable liquid back to the nonvolatile ionic liquid.

17. The non-transitory computer-readable medium according to claim **16**, wherein the nonvolatile ionic liquid is a room-temperature ionic liquid.

18. The non-transitory computer-readable medium according to claim **16**, wherein the nonvolatile ionic liquid produces and releases one or more of 1-ethyl-3-methyl- and 1-butyl-3-methyl-on application of the voltage across the nonvolatile ionic liquid.

19. The non-transitory computer-readable medium according to claim **16**, further comprising:

applying at least 6 volts to the nonvolatile ionic liquid to convert the nonvolatile ionic liquid into the flammable liquid from a power source.

20. The non-transitory computer-readable medium according to claim **16**, further comprising:

applying 6 volts to 40 volts to the nonvolatile ionic liquid to convert the nonvolatile ionic liquid into the flammable liquid.

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