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(54) **GAS STREAM PURIFICATION METHOD UTILIZING ELECTRICALLY DRIVEN OXYGEN ION TRANSPORT**

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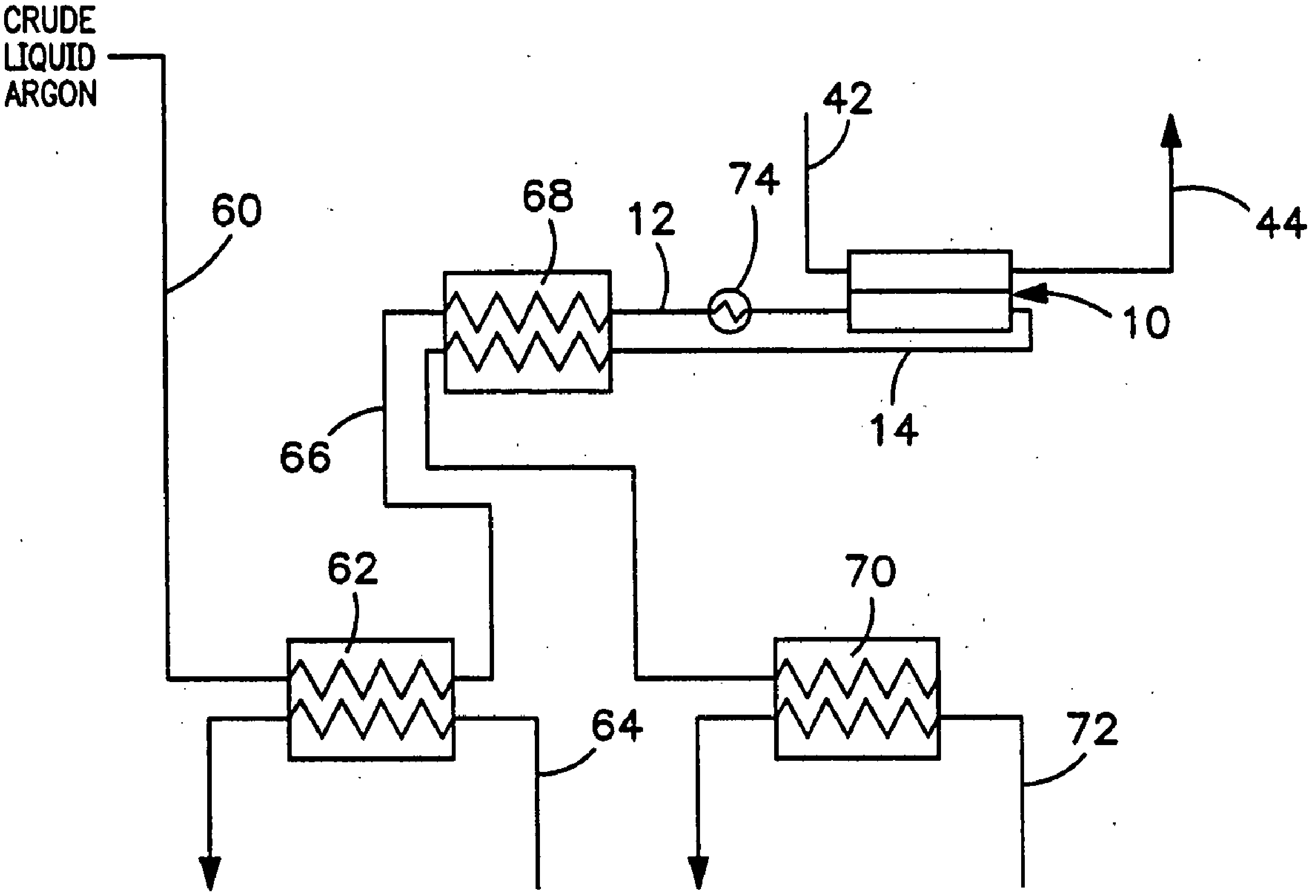
(57) **ABSTRACT**

A method of purifying a gas stream by removing oxygen from the gas stream in which the gas stream is introduced into a series of electrically driven oxygen separation zones that separate the oxygen from the gas stream. Each of the electrically driven oxygen separation zones has an electrolyte that conducts oxygen ions upon the application of the voltage to electrodes sandwiching the electrolyte. The voltage applied to each of the electrodes of the separation zones is selected such that an ionic current induced in the electrolyte within a particular zone that is no greater than a limiting current. When voltage is applied in such manner, the electrical power that is consumed is reduced over the power that would otherwise be consumed had a constant voltage been applied to all zones. The gas stream can be a crude argon stream obtained from a crude argon column or a crude nitrogen stream obtained from a pressure swing adsorption unit or a polymeric membrane unit.



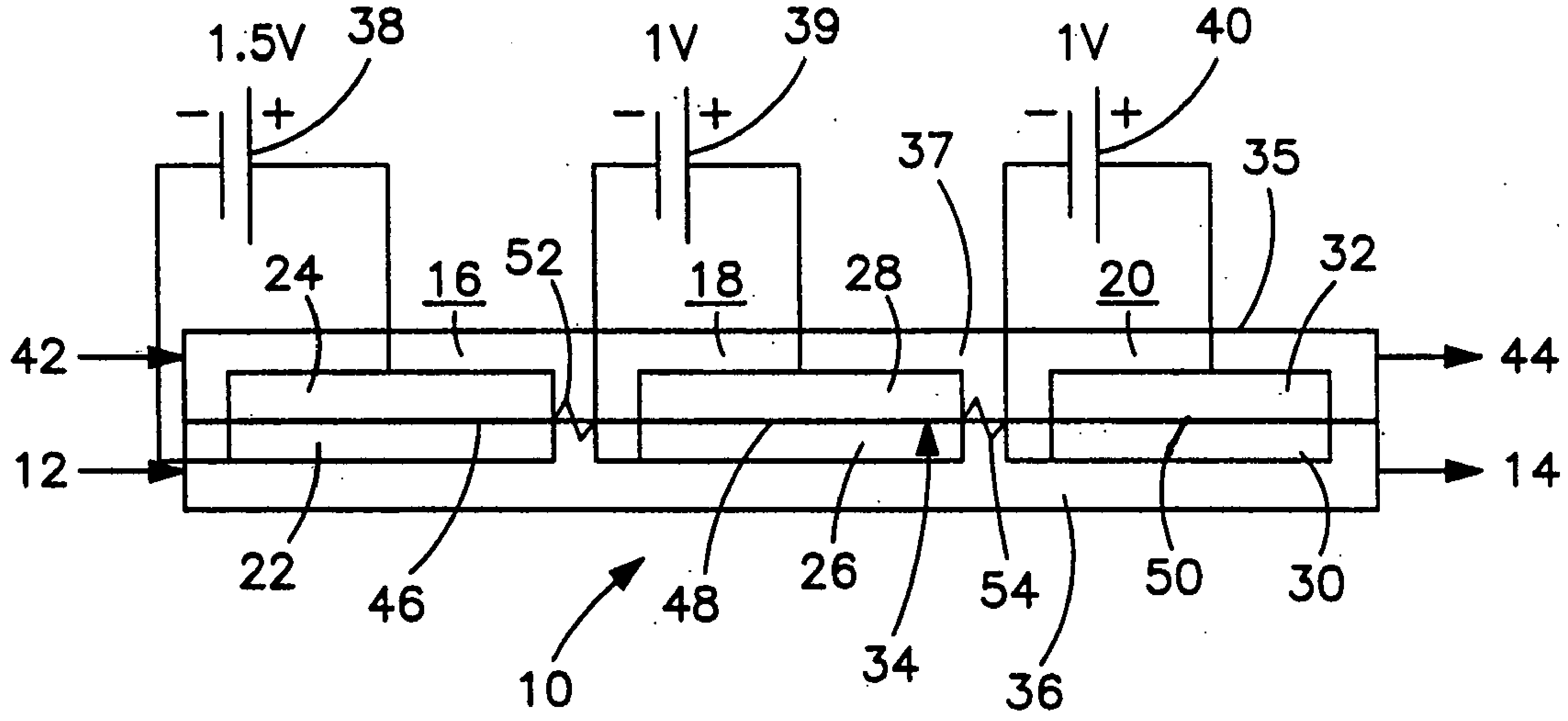

1.5V
38
−
+
1V
39
−
+
1V
40
−
+
37
35
24
16
52
18
28
20
32
42
44
12
14
22
46
10
48
26
34
54
36
50
30

FIG. 1

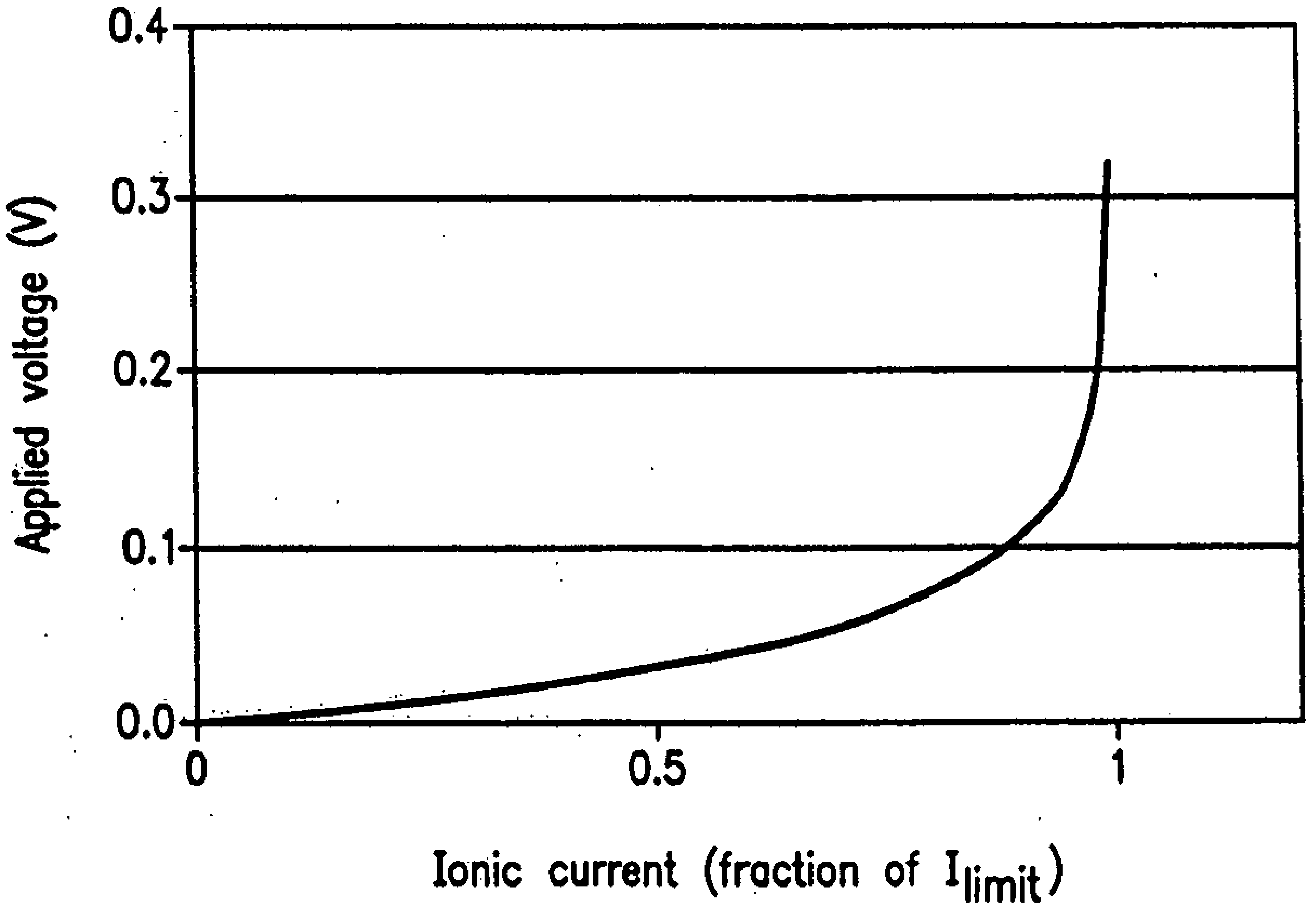

Applied voltage (V)
0.4
0.3
0.2
0.1
0.0
0
0.5
1
Ionic current (fraction of I_{limit})

FIG. 2

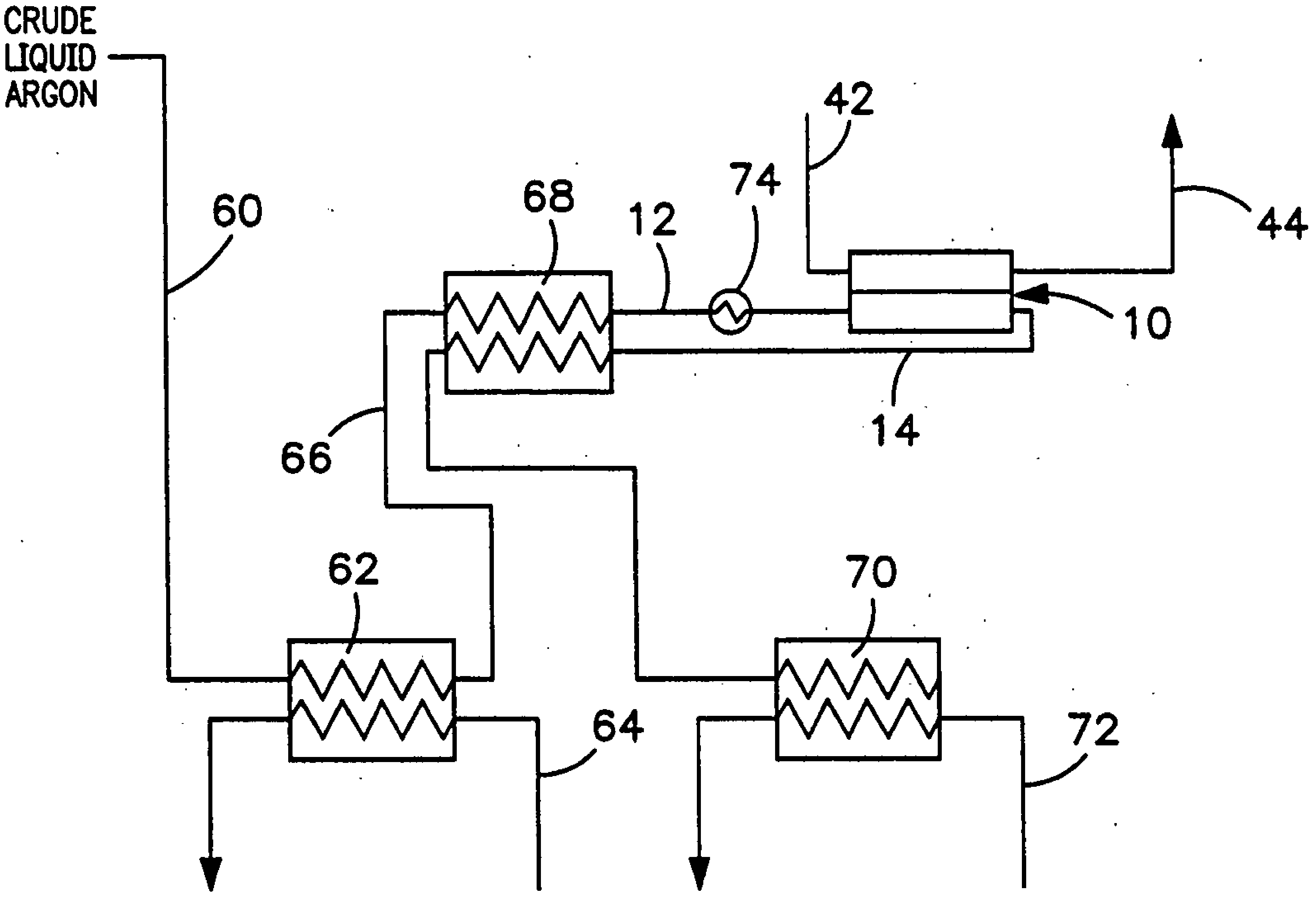

CRUDE LIQUID ARGON
60
68
12
74
42
44
10
14
66
62
70
64
72

FIG. 3

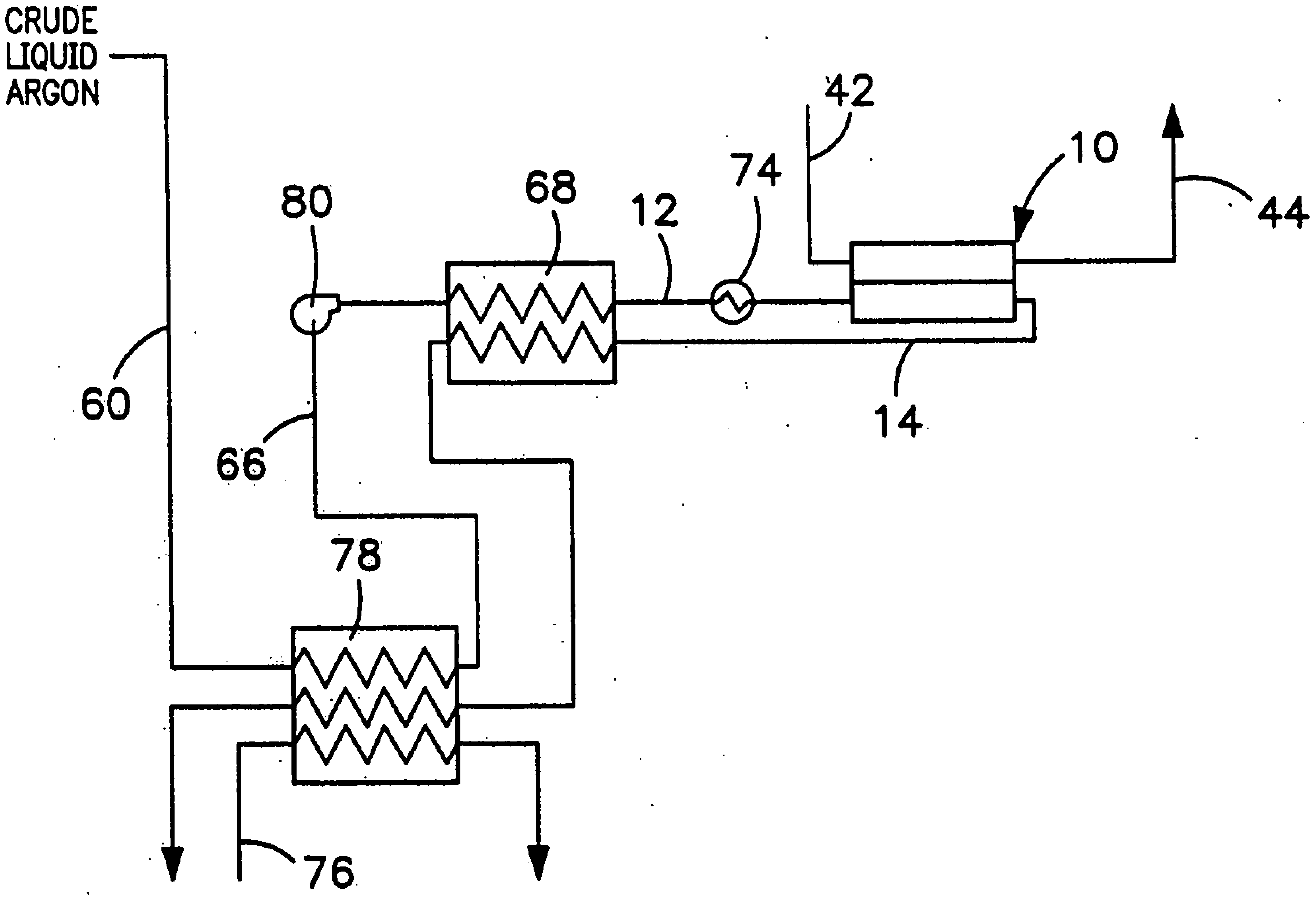

CRUDE LIQUID ARGON
42
10
44
80
68
12
74
60
66
14
78
76

FIG. 4

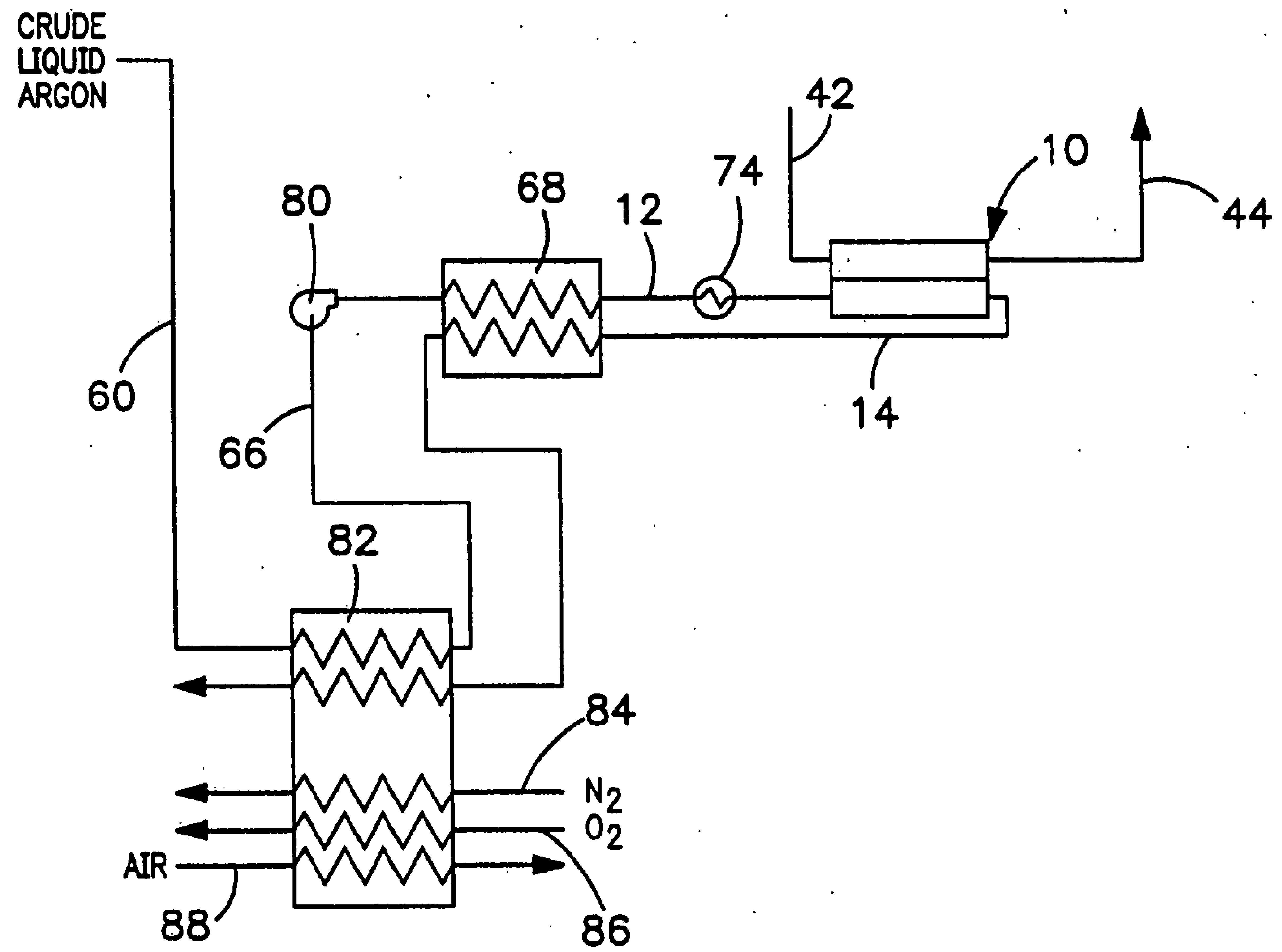

CRUDE LIQUID ARGON
42
10
44
74
80
68
12
60
66
14
82
84
N₂
O₂
AIR
88
86

FIG. 5

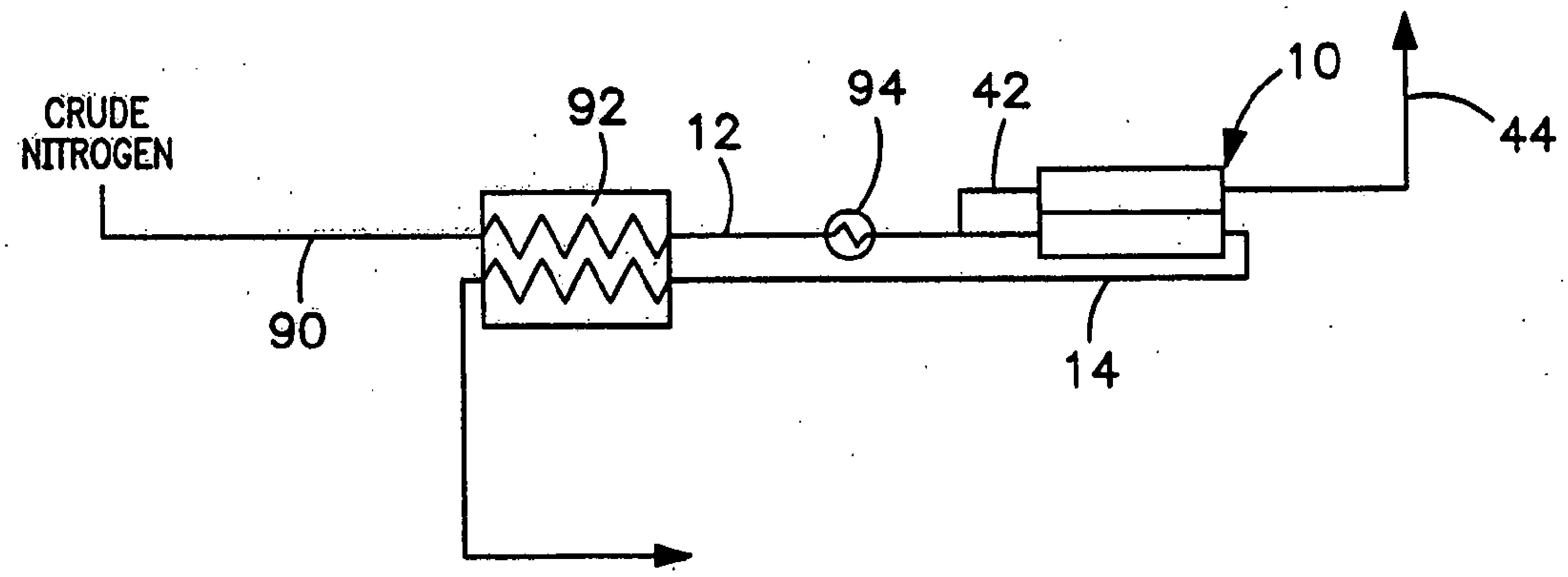

CRUDE NITROGEN
92
12
94
42
10
44
90
14

FIG. 6

GAS STREAM PURIFICATION METHOD UTILIZING ELECTRICALLY DRIVEN OXYGEN ION TRANSPORT

FIELD OF THE INVENTION

[0001] The present invention relates to a method of purifying a gas stream in which the gas stream is introduced into a series of electrically driven oxygen separation zones having one or more oxygen ion conducting electrolytes to separate oxygen from the gas stream. More particularly, the present invention relates to such a purification method in which voltages are applied to each of the separation zones to induce an oxygen ion current that approaches a limiting value beyond which a further increase in voltage will not produce an increase in oxygen separation.

BACKGROUND OF THE INVENTION

[0002] Electrically driven oxygen transport membranes are utilized to purify feeds by separating oxygen. Such membranes employ an electrolyte which is normally an ionic conductor such as gadolinium doped ceria or yttrium stabilized zirconia. If the electrolyte is subjected to an elevated temperature and an electric potential is applied to electrodes sandwiching the electrolyte, oxygen will ionize at an electrode that serves as a cathode to produce oxygen ions. The oxygen ions will permeate through the membrane and emerge at the anode electrode. The oxygen ions combine to form elemental dioxygen and in so doing, give up excess electrons to the anode electrode.

[0003] Electrically driven oxygen separation devices have been utilized to purify crude argon streams. Crude argon is produced by the cryogenic distillation of air. In cryogenic distillation, an air stream is compressed, purified and cooled to at or near its dew point. The cooled air stream is introduced into a double column arrangement having higher and lower pressure columns connected to one another in a heat transfer relationship by a condenser-reboiler. The compressed and purified air is successively refined in the higher and lower pressure columns into oxygen and nitrogen rich fractions. A vapor stream, comparatively rich in argon, is withdrawn from the lower pressure column and introduced into a crude argon column to produce an argon rich tower overhead. The argon column is refluxed by condensing tower overhead and part of the liquid condensate is withdrawn as the crude argon stream.

[0004] In U.S. Pat. No. 5,557,951 a crude liquid argon stream is vaporized and heated. The resultant heated stream is then introduced into an electrically driven oxygen transport membrane unit to remove oxygen from the heated stream and thereby to produce a purified argon stream.

[0005] In U.S. Pat. No. 5,035,726 low pressure crude argon stream is warmed and compressed. The compressed stream is further heated and fed to an electrically driven oxygen transport membrane unit to remove the bulk of the oxygen. The resultant purified gas stream is then introduced into a distillation column for removal of nitrogen. Liquefied oxygen is withdrawn from the bottom of such column.

[0006] U.S. Pat. No. 5,454,923 illustrates a further inert gas purification system utilizing an electrochemical cell having a non porous electrolyte membrane coated with electrodes and heated to high temperatures.

[0007] The electrical power usage of any electrically driven oxygen transport membrane device is important in determining whether such operations will be economically feasible for purification purposes. This problem is particularly critical in purifying crude argon because a major expense in the cryogenic rectification of air arises from electrical power consumed, principally in the compression of the air. Therefore, the power consumption of an electrically driven oxygen separator and its use in purifying crude argon is critical to the profitability of an air separation plant making argon. The same problem pertains to other gas purification systems, for example, purification of crude nitrogen streams produced by a pressure swing adsorption unit utilizing an adsorbent bed or a membrane system employing a polymeric membrane. Both types of units also consume electricity in compressing air and hence, power consumption is an important factor in the utilization of an electrically driven oxygen separator used for purifying crude nitrogen streams obtained from such sources. As will be discussed, the present invention provides a purification method that minimizes the use of electrical power for a specific size of an electrically driven oxygen separator.

SUMMARY OF THE INVENTION

[0008] The present invention provides a method of purifying a gas stream by removing oxygen from the gas stream. In accordance with the method, the gas stream is introduced into a series of electrically driven oxygen separation zones that operate at an elevated temperature to separate the oxygen from the gas stream. The separation of oxygen produces a purified gas stream. Each of the electrically driven separation zones has an electrolyte and cathode and anode assemblies for applying a voltage to the electrolyte such that the oxygen ions are transported through the electrolyte and emerge therefrom to recombine into elemental oxygen. This separates the oxygen from the gas stream to produce the purified gas stream.

[0009] The oxygen is separated from the gas stream at a successively lower partial pressure due to the separation of the oxygen within the successive electrically driven oxygen separation zones. Each of the electrically driven separation zones is capable of separating the oxygen as an increasing function of the voltage applied to the cathode and anode assemblies up to a level that induces an oxygen ion current that approaches a limiting oxygen ion current within the electrically driven oxygen separation zones. At the limiting oxygen ion current, a further increase in voltage fails to produce an increase in oxygen separation. The limiting oxygen ion current is a function of the successively lower partial pressure such that the voltage applied decreases for each of the successive electrically driven oxygen separation zones. The voltage is applied to each of the electrically driven oxygen separation zones in an amount selected such that the oxygen ion current approaches the limiting oxygen ion current applicable thereto.

[0010] In the prior art, constant voltage is applied to the electrically driven oxygen separation zone. However, as the gas stream traverses the device, it becomes evermore dilute in oxygen. As a result, the oxygen partial pressure decreases. Thus, a voltage is not optimally being applied because as the gas to be treated passes through the membrane, the partial pressure of the gas decreases and the same voltage is not necessary. Separately applying voltages so that the oxygen ion current approaches the limiting value in downstream zones of separation thereby reduces the overall power consumption of the membrane for a specific size of membrane required for a particular application.

[0011] The present invention has application to the purification of crude argon streams by removing oxygen from such streams. If the gas stream is a crude argon stream, the gas stream is formed by vaporizing a crude liquid argon stream withdrawn from a crude argon column of a cryogenic air separation plant and containing the oxygen in a range of between about 0.1 percent and about 3 percent by volume. Preferably, the crude liquid argon stream contains between 0.5 percent and about 2 percent by volume.

[0012] A further application of the present invention relates to the purification of gas streams that constitute crude nitrogen streams withdrawn from pressure swing adsorption units or membrane separation units. In such case, the crude nitrogen stream can contain between about 0.05 percent and about 2 percent by volume oxygen. More preferably, the crude nitrogen stream contains between about 0.1 percent and about 1 percent by volume oxygen and most preferably, the crude nitrogen stream contains between about 0.15 percent and about 0.5 percent by volume oxygen.

[0013] The oxygen ion current can be between about 80 percent and about 99.99 percent of the limiting oxygen ion current. In preferred modes of operation of the present invention, the oxygen ion current is at least about 95 percent of the limiting oxygen ion current.

[0014] If the electrolyte is formed from YSZ, the elevated operational temperature of the electrically driven oxygen separation zones is between about 600° C. and about 900° C. A temperature range of between about 650° C. and about 800° C. is more preferred and a range of between about 700° C. and about 800° C. is particularly preferred.

[0015] The electrolyte can be a common electrolyte extending through each of the electrically driven oxygen separation zones. In such case each of the electrically driven oxygen separation zones is defined between the particular cathode and anode assemblies at which the voltage is applied. It is understood, however, that the electrically driven oxygen separation zones could be separate devices or separated from one another in the same device. As will be discussed, where the electrically driven oxygen separation zones are separated, advantageously, the initial zone could be formed from 8YSZ. The term "8YSZ" means yttria doped or stabilized zirconia containing about 8 percent by mole yttria. The successive zones could be formed from 6YSZ or 3YSZ.

[0016] In an application of the invention to the purification of crude argon, a crude liquid argon stream is vaporized through indirect heat exchange with an air stream, thereby to liquefy the air stream and thereby to form the crude argon gas stream to be purified. The crude argon gas stream is heated through indirect heat exchange with the purified gas stream and the purified gas stream is liquefied through indirect heat exchange with a liquid air stream.

[0017] Alternatively, the crude liquid argon stream, the purified gas stream and a liquid nitrogen stream are subjected to indirect heat exchange, thereby to vaporize the crude liquid argon stream to form the crude argon stream to be purified, to vaporize the liquid nitrogen stream and to liquefy the purified gas stream. The resultant crude argon gas stream is heated through further indirect heat exchange with the purified gas stream prior to the purified gas stream engaging in the heat exchange involving the purified gas stream and the crude liquid argon stream. Further pressure is imparted to the crude argon stream by a blower to raise the pressure thereof above that of the purified gas stream to provide a better match of heating and cooling curves for the heat exchange between the liquid and gas streams.

[0018] In yet a further alternative, the present invention provides vaporizing the crude liquid argon stream and liquefying the product stream in a main heat exchanger of a cryogenic air separation plant. The crude argon stream can be heated through indirect heat exchange with the purified gas stream prior to liquefaction of the purified gas stream within the main heat exchanger. A compressed and purified air stream to be rectified in the cryogenic air separation plant can be cooled within the main heat exchanger and oxygen and nitrogen product streams of the cryogenic air separation plant can be warmed within the main heat exchanger.

[0019] In an application of the present invention to the purification of crude nitrogen streams, the gas stream and the purified gas stream are subject to indirect heat exchange to heat the gas stream and cool the purified gas stream. During start-up or maintenance of the electrically driven oxygen separation unit, the pressure swing adsorption unit or the membrane separation unit can be operated at a lower capacity to produce the crude nitrogen stream at a higher purity than operations conducted at full capacity.

[0020] In either of the above applications for purifying crude argon or purifying crude nitrogen, a trim heater can be employed to further heat the gas stream prior to treatment within the electrically driven oxygen separation zones.

[0021] In any embodiment of the present invention, the oxygen separated from the gas stream can be extracted with a purge stream. In case of an application of the present invention involving the purification of a crude nitrogen stream, the purge stream can be formed from part of the gas stream to be purified.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022] While the specification concludes with claims distinctly pointing out the subject matter that Applicants regard as their invention, it is believed that the invention will be better understood when taken in connection with the accompanying drawings in which:

[0023] **FIG. 1** is a schematic illustration of an oxygen separation device in accordance with the present invention;

[0024] **FIG. 2** is a graphical representation of applied voltage versus ionic current as a fraction of the limiting ionic current in an electrically driven oxygen separation device;

[0025] **FIG. 3** is a schematic illustration of the use of the oxygen separation device illustrated in **FIG. 1** applied to the purification of crude argon;

[0026] **FIG. 4** is an alternative embodiment of **FIG. 3**; **FIG. 5** is an alternative embodiment of **FIG. 4**; and

[0027] **FIG. 6** is a schematic illustration of the use of the oxygen separation device illustrated in **FIG. 1** applied to the purification of crude nitrogen.

[0028] In order to avoid needless repetition in the explanation of the accompanying Figures, the same reference numerals were used to indicate like components and streams not requiring a different explanation or description.

DETAILED DESCRIPTION

[0029] With reference to **FIG. 1** an electrically driven oxygen separation device **10** is illustrated that is designed to purify a gas stream **12** to produce a purified gas stream **14** through separation of oxygen from gas stream **12**. The oxygen is separated within electrically driven oxygen separation zones **16**, **18** and **20** that are defined by three cathode and anode assemblies having cathode and anode electrodes **22**, **24**; **26**, **28** and **30**, **32**, respectively. Although not illustrated, but as would be known to those skilled in the art, the cathode and anode assemblies would also be provided with conventional current collectors. Said electrodes and current collectors are all porous and sandwich an electrolyte **34**, which as will be discussed may have separate sections. The cathode and anode assemblies and electrolyte **34** are housed within a casing **35** to define passageways **36** and **37** on opposite sides of electrolyte **34**. It is to be noted as used herein and in the claims, the term "cathode and anode assemblies" means porous cathodes and anodes and associated porous current collectors.

[0030] Electrodes **22**, **24**; **26**, **28**; and **30**, **32** are so named in that they consist of electrically conductive materials. Conventional current collectors form outer layers of the electrodes and are in turn connected to direct current electrical power sources **38**, **39** and **40**. As illustrated, different voltages are applied to cathode electrodes and anode electrodes **22**, **24**; **26**, **28**; and **30**, **32** by electrical power sources **38**, **39** and **40** such that the oxygen within gas stream **12** passing through passageway **36** ionizes at the juncture of pores within cathodes **22**, **26** and **30** and the electrolyte **34** and the resultant oxygen ions are transported through the electrolyte **34** to anode electrodes **24**, **28** and **32**. The oxygen ions combine at the juncture of pores within anode electrodes **24**, **28** and **32** and electrolyte **34** to form elemental dioxygen. The resultant free electrons are conducted within anodes **24**, **28** and **32** back to electrical power sources **38**, **39** and **40**. The oxygen is extracted by way of a purge gas stream **42** introduced into passageway **37** to sweep and remove the oxygen from electrically driven oxygen separation device **10**. Purge gas stream **42** can be nitrogen or other inert gas containing less than about 21 percent oxygen. Other known extraction means can be employed such as vacuum extraction. Purge gas stream **42** is discharged as oxygen containing purge gas stream **44**.

[0031] In the illustrated embodiment, the electrolyte **34** is of tubular configuration, about 0.5 mm thick, about 6.3 mm in outside diameter and has an overall length of about 91 cm to provide a surface area of about 160 cm^2. The cathodes **22**, **26** and **30** are fabricated from a mixture of 50 wt % lanthanum strontium manganite ($La_{0.8}Sr_{0.2}MnO_{3\pm\delta}$) and 50 wt % yttria-stabilized zirconia ($Zr_{0.85}Y_{0.15}O_{1.925}$). Each are between about 10 and about 30 microns thick, have an average pore size of 10 microns and a porosity of about 40 percent. In this regard, average pore size is measured by image analysis of scanning electron micrographs. The current collector can be silver and have a thickness of between about 50 and about 100 microns, a pore size of about 10 microns and a porosity of about 40 percent. The anodes **24**, **28** and **32** are fabricated from a mixture of 50 wt % lanthanum strontium manganite ($La_{0.8}Sr_{0.2}MnO_{3+\delta}$) and 50 wt % yttria-stabilized zirconia ($Zr_{0.85}Y_{0.15}O_{1.925}$). Each of the anodes are about 20 micron thick, have pores with a pore size of about 5 micron and a porosity of about 40 percent.

[0032] The assemblies of cathode and anode electrode **22**, **24**; **26**, **28** and **30**, **32**, divide the electrolyte into three equal portions **46**, **48** and **50** with gaps **52** and **54** of about 1 cm between each of the same. In this regard, the gaps are spacers that can be fabricated of YSZ and connected to portions **46**, **48** and **50** by glass sealing, brazing or other bonding and sealing technique. As can be appreciated, casing **35** could thus be fabricated from three separate sections with flow connection between said sections for the passage of gas stream **12** and purge gas stream **42** on opposite sides of the electrolyte. Moreover, although electrolyte **34** is shown as broken up into three portions **46**, **48** and **50**, **46**, in a possible embodiment of the present invention, electrolyte **34** could be common to all electrically driven oxygen separation zones **16**, **18** and **20** with no gaps.

[0033] The actual voltage that is applied across the electrolyte **34** has to be greater than the Nernst potential due to a difference in the oxygen partial pressure on the anode and cathode side in order for oxygen to be removed from gas stream **10**. The Nernst potential is described by the following equation:

$$V_{Nernst} = \frac{R \cdot T}{4 \cdot F} \cdot \log_e \left(\frac{pO_2 \text{ on anode side of } OTM \text{ membrane}}{pO_2 \text{ on argon side of } OTM \text{ membrane}} \right)$$

In this equation, R is the gas constant, T is the temperature in Kelvin, F is Faraday's constant and "pO_2" is the partial pressure of oxygen.

[0034] The upper limit of the voltage that can be possibly applied is a voltage that will cause failure of electrolyte **34** due to electrochemical reduction. Electrochemical reduction can induce electronic conductivity into electrolyte **34** rendering it electrically inefficient for oxygen ion conduction. Additionally, such reduction can also cause isothermal expansion which will generate stresses in electrolyte **34** that can be sufficient to cause it to fracture. Typically, the maximum voltage is 2 volts. However, as will be discussed, the voltage that should be applied in each of the electrically driven oxygen separation zones **16**, **18** and **20** and portions **46**, **48** and **50** of electrolyte **34** should be much less than the ultimate limit.

[0035] With reference to **FIG. 2**, a graphical representation is illustrated of applied voltage versus ionic current as a fraction of a limiting ionic current that is induced within electrolyte **34**. The ionic current is a measure of the ionic flux passing through electrolyte **34** per unit area and is analogous of the flux of electrons passing through a conductor to measure an electrical current. The behavior of applied voltage illustrated in **FIG. 2** is governed by the following equation:

$$V_{applied} = \frac{R \cdot T}{4 \cdot F} \cdot \log_e\left(1 - \frac{I_{ionic}}{I_{limit}}\right)^n$$

In this equation, R is the gas constant, T is the temperature in Kelvin, F is the Faraday constant, and I is current.

[**0036**] As the applied voltage is increased, a point is reached in which a limiting ionic current exists. A further increase in voltage will not increase the degree of separation. This limit to the ionic current is a function of partial pressure. As such, as the partial pressure decreases, the limiting ionic current decreases and therefore, in accordance with the present invention, the voltage to be applied should decrease. For example, in case of an argon stream containing 2 percent oxygen, a voltage of 2 volts can be applied without reaching a limiting current. However, as oxygen is removed from the argon stream down to 100 parts per million, then a limiting current can be observed when a voltage of approximately 0.6 volts is applied. The particular value of the limiting current and the applied voltage that results in the limiting current is a complicated function of the temperature, the oxygen partial pressure on either side of the electrolyte, the composition of the atmosphere on either side of the electrolyte, the electrochemical performance, the size of the electrolyte, the microstructure of electrodes on either side of the electrolyte and the particular electrochemical mechanism that is giving rise to the limiting current behavior.

[**0037**] Due to the complexity in accurately determining the limiting voltage, in electrically driven oxygen separation device **10**, particular values of voltage applied to each of electrically driven oxygen separation zones **16**, **18** and **20** is best determined by experiment. In such an experiment, an oxygen analyzer is placed downstream of the particular zone and successively higher voltages are applied until a decrease in oxygen concentration is not observed. The accuracy of such experiment will of course determine the number or size of step increases in voltage that are applied until the limiting voltage is achieved. For example, 0.01 voltage steps will determine the limiting voltage within one percent while 0.001 voltage steps will determine the limiting voltage within 0.1 percent.

[**0038**] Preferably the applied voltage can be chosen as to result in an oxygen ion current that is between about 80 percent and about 99.9 percent of the oxygen ion limiting current. In any embodiment it is preferred, however, that the oxygen ion current induced in an electrolyte is at least about 95 percent of the oxygen ion limiting current.

[**0039**] By way of a calculated example, power source **38** applies 1.5 volts between cathode electrode **22** and anode electrode assembly **24** within zone **16**. Assuming that an argon stream or a crude nitrogen stream is to be purified that contains roughly 1.8 percent oxygen, a significant amount of the oxygen will be removed within zone **16** so that the stream exiting **16** and entering **18** should contain approximately 1000 parts per million oxygen. Power source **39** supplies about 1 volt between cathode and anode electrodes **26** and **28** within zone **18** and the stream exiting zone **18** should contain roughly 100 parts per million oxygen. Power source **40** applies 0.5 volts between cathode and anode electrodes **30** and **32** so that purified gas stream **14** has an oxygen concentration of about 10 parts per million. As can be appreciated, had 1.5 volts been applied throughout electrochemical device **10** much more power would have been consumed.

[**0040**] Where significant quantities of oxygen are present within gas stream **12**, the total electrochemical performance of electrolyte **34** is governed by the performance of electrolyte **34** and assemblies of the cathodes and anodes. Preferably, under such conditions the electrolyte **34** should have a high oxygen ion conductivity. 8 mole percent yttria doped zirconia (8YSZ, $Zr_{0.852}Y_{0.148}O_{1.926}$) is preferred. Other electrolyte material such as gadolinium doped ceria and lanthanum strontium gadolinium magnesium oxide are possible materials because they possess even higher ionic conductivity than 8YSZ. However the increased cost and lower strength of these materials outweigh their improved electrochemical performance in a practical device.

[**0041**] The resistance of the electrolyte is a function of the oxygen partial pressure and the resistance in the cathode is proportional to the oxygen partial pressure according to the following equation:

$$R_{cathode} \propto pO_2^{1/n};$$

where n is an experimentally determined number between 1 and 4, inclusive. As the oxygen content of the argon stream is reduced, then the electrochemical performance becomes increasingly dependent upon the resistance of the electrodes, particularly the cathode which is in direct contact with the crude argon and less dependent on the performance of the electrolyte. Under these conditions it is advantageous to use an electrolyte material with a lower ionic conductivity but improved strength such as 6 mole percent yttria doped zirconia (6YSZ, $Zr_{0.886}Y_{0.114}O_{1.943}$) or 3 mole percent yttria doped zirconia (3YSZ, $Zr_{0.942}Y_{0.058}O_{1.971}$). Thus, in electrically driven oxygen separation device **10** applied to purifying crude argon, portion **46** of electrolyte **34** can be fabricated from 8 mole percent yttria doped zirconia ("8YSZ") and portions **48** and **50** can be fabricated from either 6 or 3 mole percent yttria doped zirconia.

[**0042**] If a YSZ electrolyte is used, then, preferably, the membrane will operate somewhere between 600° C. and about 900° C., more preferably between about 650° C. and about 850° C. and most preferably between 700° C. and about 800° C.

[**0043**] With reference to **FIG. 3**, electrically driven oxygen separation device **10** is shown as an oxygen purifier to purify a crude liquid argon stream **60** obtained from an air separation unit. In such an air separation unit, an air stream is compressed, purified and cooled to at or near its dew point. The cooled air stream is introduced into the bottom of a higher pressure column to produce a crude oxygen column bottoms and a nitrogen rich overhead. The resulting tower overhead is condensed and further refined in a lower pressure column that produces an oxygen rich column bottoms and a nitrogen rich tower overhead. The oxygen rich liquid column bottoms serves to condense the tower overhead produced in the higher pressure column and the crude liquid oxygen produced in the higher pressure column is expanded and used to condense tower overhead in the lower pressure column. A vapor stream having an argon concentration within the range of between about 5 and about 25 percent is withdrawn from the lower pressure column and introduced into the bottom of a crude argon column. The crude argon column operates as a stripping column so that the argon content of the vapor increases as the vapor rises within the column and contacts a descending liquid phase. The liquid phase thereby becomes evermore enriched in oxygen during its descent within the column. A product stream can be withdrawn from the top of the argon column as a liquid to form the crude liquid argon stream **60**. The liquid column bottoms is returned to the lower pressure column.

[0044] Crude liquid argon stream **60** preferably has an oxygen concentration of between about 0.1 percent and about 3 percent by volume. More preferably, crude liquid argon stream **60** has an oxygen concentration of between about 0.5 percent and about 2 percent by volume. The reason for such ranges is that typically crude liquid argon has an oxygen concentration of about 3 percent by volume and with limited added expense, the oxygen concentration in the crude liquid argon stream can be reduced by a slight increase in the number of stages. The reduced oxygen content reduces the amount of power required for electrically driven oxygen separation device **10**.

[0045] Crude liquid argon stream **60** is vaporized within a heat exchanger **62** through indirect heat exchange with an air stream **64** that is thereby liquefied. The resultant gaseous crude argon stream **66** is introduced into a heat exchanger **68** to form gas stream **12** that is introduced into electrically driven oxygen separation device **10** to produce purified gas stream **14**. Purified gas stream **14** exchanges heat with gaseous crude argon stream **66** within heat exchanger **68** so that gas stream **12** to be purified possess a temperature at or near the operational temperature of electrically driven oxygen separation device **10**. Purified gas stream **14** after passage through heat exchanger **68** is cooled to ambient or near ambient temperatures as a result of such heat exchange. Purified gas stream **14** is then introduced into a heat exchanger **70** in which the purified gas stream **14** liquefies through indirect heat exchange with a liquid air stream **72** that can be extracted from the higher pressure distillation column. A trim heater **74** can be provided so that gas stream **12** upon its introduction into electrically driven oxygen separation device **10** is exactly at operational temperature. As indicated above, a purge gas stream **42** is introduced into electrically driven oxygen separation device **10** to extract the separated oxygen.

[0046] **FIG. 4** is an alternative embodiment of **FIG. 3**. In order to avoid needless repetition of explanation, the same reference numbers have been used in **FIG. 4** for elements that have the same description as set forth above for **FIG. 3**. In **FIG. 4**, crude liquid argon stream **60** vaporizes along with a liquid nitrogen stream **76** within a heat exchanger **78** to in turn liquefy purified gas stream **14**. Purified gas stream **14** is at a lower pressure than that of crude liquid argon stream **60** and therefore, a thermal mismatch exists that would not permit purified gas stream **14** to otherwise vaporize crude liquid argon stream **60**. However, by adding a blower **80** to slightly raise the pressure of the resultant vaporized crude argon stream **66** and the provision of liquid nitrogen stream **76**, crude liquid argon stream **60** will vaporize as required and purified gas stream **14** will liquefy without an excessive requirement for liquid nitrogen that would make the entire process unprofitable.

[0047] With reference to **FIG. 5**, In a yet further embodiment, crude liquid argon stream **60** and purified gas stream **14** are introduced into a main heat exchanger **82** of a cryogenic air separation plant. In main heat exchanger **82** crude liquid argon stream **60** vaporizes and product stream **14** after having been cooled in heat exchanger **68** liquefies. Main heat exchanger **82** is conventionally provided with passages for nitrogen and oxygen product streams **84** and **86** to warm such streams. For example, nitrogen product stream **84** could be made up of tower overhead produced in a lower pressure column of such cryogenic air separation plant and oxygen product stream **86** could be liquid oxygen or oxygen vapor made up of oxygen produced as column bottoms within the lower pressure column. A further passage is also provided for a compressed and purified air stream **88** that is cooled within main heat exchanger **82** to a temperature at or near its dew point for introduction into the bottom region of a higher pressure column for rectification of the air. The flow rates of crude liquid argon stream **60** and product gas stream **14** are of such lesser magnitudes than the other streams passing through main heat exchanger **82**, that the foregoing can be effectuated by a retrofit modification of an existing main heat exchanger without any significant effect on its performance. Optionally, a blower **80** can be provided to provide a better match between heating and cooling curves of product gas stream **14** and crude liquid argon stream **60**.

[0048] In the embodiments illustrated in **FIGS. 3, 4** and **5**, the illustrated gas streams are sufficiently pressurized to flow through the heat exchangers by provision of a liquid head being built up within crude liquid argon stream **60** by locating the argon column from which crude liquid argon stream **60** is taken above grade.

[0049] With reference to **FIG. 6**, electrically driven oxygen separation device **10** is shown as an oxygen purifier to purify a crude nitrogen stream **90** obtained from a pressure swing adsorption unit or a membrane unit. As well known in the art, a pressure swing adsorption unit has beds of adsorbent that can be formed of carbon molecular sieve material. The air is compressed and passed through an adsorbing bed to adsorb oxygen contained in the air to produce the crude nitrogen stream **82**. While this is occurring at least another bed is off-line and being regenerated by allowing oxygen to desorb from the adsorbent contained in such bed at a lower pressure. Part of the regeneration can occur by pressure equalization with yet other beds and various purge steps that can involve purging the bed to be regenerated with some of the product. After the bed is fully regenerated, it can be brought back on line to produce a product. In membrane separation units a compressed air stream is contacted with a polymeric membrane that is made of material selected to pass oxygen faster than nitrogen to produce a permeate stream rich in oxygen and a nitrogen retentate stream that forms the crude nitrogen stream **82**.

[0050] Crude nitrogen stream **90** is heated within a heat exchanger **92** through indirect heat exchange with product gas stream **14** to form gas stream **12** that is introduced into electrically driven oxygen separation device **10** to produce purified gas stream **14**. Gas stream **12** as a result of such heat exchange possesses a temperature near the operational temperature of electrically driven oxygen separation device **10**. A trim heater **94** can be used for final heating of gas stream **12** to the operational temperature of electrically driven oxygen separation device **10**. Purified gas stream **14** after passage through heat exchanger **92** is cooled to ambient or near ambient temperatures as a result of such heat exchange. Additionally part of the gas stream **12** can be used to form purge stream **42** to sweep and remove permeated oxygen from electrically driven oxygen separation device **10**.

[0051] In an exemplary mode of operation, crude nitrogen stream preferably contains about 0.5 volume percent of oxygen and is heated to about 700° C. within heat exchanger **92**. The electrically driven oxygen separation device **10** operated at about 700° C. requiring a temperature rise of 50° C. to account for atmospheric heat loss or roughly 113 watts per 100 scfh of crude nitrogen. Since, the electrically driven oxygen separation device **10** requires roughly 93 watts per 100 scfh of crude nitrogen under such operational conditions, about 20 watts per 100 scfh of crude nitrogen is required for trim heater **94** to maintain stable operating temperatures.

[0052] Crude nitrogen stream **90** preferably has an oxygen concentration of between about 0.05 percent and about 2 percent by volume oxygen. More preferably, the oxygen concentration is between about 0.1 percent and about 1 percent by volume oxygen. Most preferably, the oxygen concentration is between about 0.15 percent and about 0.5 percent by volume oxygen. It has been calculated, that a minimum power usage for electrically driven oxygen separation device **10** is achieved when crude nitrogen stream contains about 1.5 percent by volume oxygen. A minimum capital cost for the entire system, including a pressure swing adsorption unit, is realized when the crude nitrogen stream contains about 0.15 percent by volume oxygen. Overall, when the crude nitrogen stream contains between about 0.15 percent and about 0.5 percent oxygen by volume, the lowest total cost will be achieved for a 10,000 scfh system.

[0053] During start-up conditions of the electrically driven oxygen separation device **10**, the pressure swing adsorption unit or membrane separation unit should be operated at a lower capacity and therefore produce a crude nitrogen stream **90** at a lower flow rate and therefore at a higher purity. This allows the customer to receive the product while the electrically driven oxygen separation device **10** is being heated up. For most pressure swing adsorption units, during start-up, such units should be operated at about 30 percent of capacity to produce crude nitrogen stream **90** with an oxygen concentration of about 50 ppm. Also, the pressure swing adsorption unit or membrane separation unit can be operated in such manner during maintenance of any of the electrically driven oxygen separation zones **16**, **18** and **20**.

[0054] While the present invention has been described with reference to a preferred embodiment, as will occur to those skilled in the art numerous changes, omissions and additions can be made without departing from the spirit and the scope of the present invention.

We claim:

1. A method of purifying a gas stream by removing oxygen from said gas stream, said method comprising:

introducing said gas stream into a series of electrically driven oxygen separation zones operating an elevated temperature to separate the oxygen from the gas stream, thereby to produce a purified gas stream;

each of the electrically driven oxygen separation zones having an electrolyte and cathode and anode assemblies for applying a voltage to the electrolyte that such that the oxygen ions are transported through the electrolyte and emerge therefrom to recombine into elemental oxygen, thereby to separate the oxygen from the gas stream;

the oxygen being separated from the gas stream at a successively lower partial pressure due to the separation of the oxygen within successive electrically driven oxygen separation zones;

each of the electrically driven oxygen separation zones being capable of separating the oxygen as an increasing function of the voltage applied to the cathode and anode assemblies up to a level that induces an oxygen ion current that approaches a limiting oxygen ion current within the electrically driven oxygen separation zones at which a further increase in the voltage fails to produce an increase in oxygen separation, the limiting oxygen ion current limit being a function of the successively lower partial pressure such that the voltage applied decreases for each of the successive electrically driven oxygen separation zones; and

applying the voltage to each of the electrically driven oxygen separation zones in an amount selected such that the oxygen ion current approaches the limiting oxygen ion current applicable thereto.

2. The method of claim 1, wherein the gas stream is a crude argon stream that is formed by vaporizing a crude liquid argon stream withdrawn from a crude argon column of a cryogenic air separation plant and containing the oxygen in a range of between about 0.1 percent and about 3 percent by volume.

3. The method of claim 1, wherein the gas stream is a crude argon stream that is formed by vaporizing a crude liquid argon stream withdrawn from a crude argon column of a cryogenic air separation plant and containing the oxygen in a range of between about 0.5 percent and about 2 percent by volume.

4. The method of claim 1, wherein the gas stream is a crude nitrogen stream withdrawn from a pressure swing adsorption apparatus or a membrane separation apparatus and containing between about 0.05 percent and about 2 percent by volume oxygen.

5. The method of claim 1, wherein the gas stream is a crude nitrogen stream withdrawn from a pressure swing adsorption apparatus or a membrane separation apparatus and containing between about 0.1 percent and about 1 percent by volume oxygen.

6. The method of claim 1, wherein the gas stream is a crude nitrogen stream withdrawn from a pressure swing adsorption apparatus or a membrane separation apparatus and containing between about 0.15 percent and about 0.5 percent by volume oxygen.

7. The method of claim 2 or claim 4, wherein the oxygen ion current is between about 80 percent and about 99.9 percent of the limiting oxygen ion current.

8. The method of claim 7, wherein the oxygen ion current is at least about 95 percent of the limiting oxygen ion current.

9. The method of claim 2 or claim 4, wherein the electrolyte is fabricated from YSZ and the elevated temperature is in a range of between about 600° C. and about 900° C.

10. The method of claim 2 or claim 4, wherein the range is between about 650° C. and about 800° C.

11. The method of claim 3 or claim 6, wherein the range is between about 700° C. and about 800° C.

12. The method of claim 2 or claim 4, wherein:

the electrically driven oxygen separation zones are separated; and

the electrolyte of an initial of the electrically driven oxygen separation zones is fabricated from 8YSZ and subsequent of the electrically driven oxygen separation zones are fabricated from 6 YSZ or 3YSZ.

13. The method of claim 2, wherein:

a crude liquid argon stream is vaporized through indirect heat exchange with an air stream, thereby to liquefy the air stream and thereby to form the crude argon gas stream to be purified;

the crude argon gas stream is heated through indirect heat exchange with the purified gas stream; and

the purified gas stream is liquefied through indirect heat exchange with a liquid air stream.

14. The method of claim 2, wherein:

a crude liquid argon stream, the purified gas stream and a liquid nitrogen stream are subjected to indirect heat exchange, thereby to vaporize the crude liquid argon stream to form the crude argon stream to be purified, to vaporize the liquid nitrogen stream and to liquefy the purified gas stream;

the crude argon stream is heated through further indirect heat exchange with the purified gas stream prior to the purified gas stream engaging in the heat exchange involving the purified gas stream and the crude liquid argon stream stream; and

further pressure is imparted to the crude argon stream to raise the pressure thereof above that of the purified gas stream by a blower.

15. The method of claim 2, wherein:

the crude liquid argon stream is vaporized and the product stream is liquefied in a main heat exchanger of the cryogenic air separation plant; and

the crude argon stream is heated through indirect heat exchange with the purified gas stream prior to liquefaction of the purified gas stream within the main heat exchanger.

16. The method claim 15, wherein a compressed and purified air stream to be rectified in the cryogenic air separation plant is cooled within the main heat exchanger and oxygen and nitrogen product streams of the cryogenic air separation plant are warmed within the main heat exchanger.

17. The method of claim 4, wherein the gas stream and the purified gas stream are subject to indirect heat exchange to heat the gas stream and cool the purified gas stream.

18. The method of claim 4 or claim 17, wherein during start-up or maintenance of the electrically driven oxygen separation unit, the pressure swing adsorption unit or the membrane separation unit is operated at a lower capacity to produce the crude nitrogen stream at a higher purity than operations conducted at full capacity.

19. The method of claim 1 or claim 2 or claim 4 or claim 13 or claim 14 or claim 15 or claim 17, wherein the oxygen separated from the gas stream is extracted from the electrically driven oxygen separator with a purge stream formed from part of the gas stream.

20. The method of claim 1 or claim 2 or claim 4 or claim 13 or claim 14 or claim 15 or claim 17 wherein the oxygen separated from the gas stream is extracted from the electrically driven oxygen separators with a purge stream.

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