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PREPARATION OF FLUOROCARBON NITRILES

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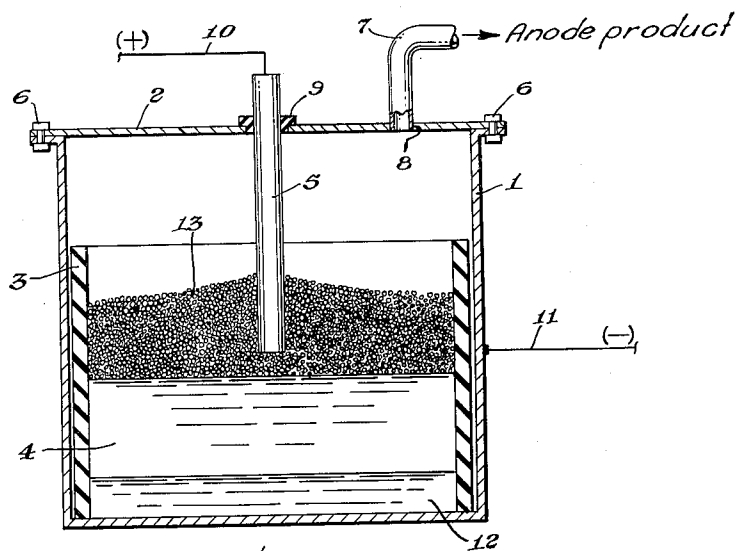


Fig. 1

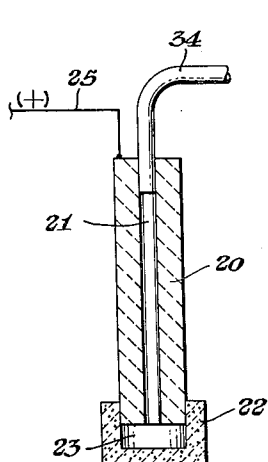


Fig. 2

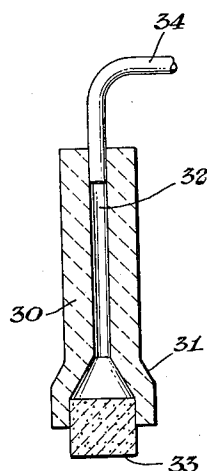


Fig. 3

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PREPARATION OF FLUOROCARBON NITRILES
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This invention relates to a process for preparation of fluorocarbon nitriles and more particularly, to the preparation of these compounds by the electrolysis of a non-volatile molten metal fluoride containing a metal cyanide or thiocyanate salt.

This application is a continuation-in-part of patent application Serial No. 663,966, filed on June 6, 1957, now abandoned.

Presently, the preparation of fluorine-containing compounds is mainly limited to fluorination of hydrocarbons and other compounds by the use of fluorinating agents, such as hydrogen fluoride and fluorine. These processes involve handling hazardous materials which are expensive and require special equipment. Metal fluorides and metal cyanides and thiocyanates are cheap raw materials and a process whereby fluorocarbon nitriles can be prepared by the electrolysis of these fused metal salts would considerably reduce the production cost of these compounds. Heretofore, no practical process was known whereby fluorocarbon nitriles could be prepared by electrolysis of fused metal fluorides.

It is, therefore, among the objects of this invention to provide a process for the preparation of fluorocarbon nitriles by electrolysis of a fused metal fluoride containing a metal cyanide or a metal thiocyanate.

The above and other objects are attained by passing an electric current through a molten electrolyte between a porous carbon anode and an insoluble cathode where the electrolyte consists essentially of a mixture of a metal fluoride which is non-volatile and stable at the electrolysis temperature and is non-wetting in respect to the anode selected from the group consisting of alkali metal fluorides, alkaline earth metal fluorides, earth metal fluorides, and mixtures thereof and a metal cyanide or a metal thiocyanate which is non-volatile and stable at the electrolysis temperature.

It has been discovered that when a porous carbon anode is used in the electrolysis of an electrolyte consisting essentially of the particular metal fluoride or fluorides and a metal cyanide or thiocyanate, an anode product is obtained containing fluorocarbon nitriles. The anode product may contain a number of fluorine-containing compounds including both saturated and unsaturated compounds other than the fluorocarbon nitriles. The anode product is gaseous at the electrolysis temperature, but higher molecular weight compound which are oils at room temperature may also be obtained. With a porous carbon anode the fluorocarbon nitriles are obtained by the electrolysis without encountering "anode effect" which heretofore had made the electrolysis of the above metal fluorides impractical.

The porous carbon anode used may be an intimately combined solid mass type which is made by combining amorphous carbon, such as petroleum coke, coal, carbon black etc. or allotropic carbon, such as graphite, with a binder and sintering the mixture to form an intimately combined solid mass having a prescribed permeability. Also, the porous anode may consist of carbonaceous material in particulate form confined so that the individual particles are in electrical contact with each other. A porous carbon anode which is intimately combined by sintering to form a solid porous cohered mass is generally preferred.

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A solid mass type porous anode having a permeability of at least one and not greater than 40 is generally used. It is preferred that the permeability be in the range of 4 to 20. While an anode having a permeability less than one may be used in special cases, no beneficial advantage is obtained. The maximum anode current density which may be used without encountering anode effect is proportional to the permeability, increasing with an increase in permeability. With the permeabilities generally used, in the range of 1 to 40, normally all practical anode current densities may be used without encountering this objectionable phenomenon. In special cases, however, where relatively low current densities are to be employed an anode having a permeability as low as 0.2 may be used, if desired. An anode having a permeability greater than 40 is seldom used. The structural strength of the anode decreases with the porosity which makes it less desirable than a less porous anode.

"Permeability" as used herein, refers to the porous anodes which are intimately combined in a solid mass by sintering and is expressed as the amount of air passing through the porous carbon anode in cubic feet per minute per square foot per inch thickness at a pressure differential of 2 inches of water. The term "porous," as used herein, means gas permeable.

While the current efficiency and the yield of fluorocarbon nitriles may not be as great, a porous anode comprising of carbonaceous material in particulate form loosely confined is less costly and thus may be desirable in some cases. Practically any carbonaceous material in particulate form may be used. Charcoal, coke, lamp black, powdered carbon, and powdered graphite are illustrative examples of some of the carbonaceous materials which are operative. Due to its availability petroleum coke in particulate form is preferred. Generally particles of the carbonaceous material larger than one inch are not used except in a large unit where a large bed is employed. Particles as small as those passing through a No. 200 standard mesh screen and being retained on a No. 300 mesh screen are operative. However, it is preferred to use carbonaceous material which will pass through a No. 6 standard mesh screen and be retained on a No. 40.

The invention may be more easily understood when the detailed discussion is considered in conjunction with the drawings, in which:

FIGURE 1 diagrammatically illustrates an electrolytic cell employing a porous anode comprising of carbonaceous material in particulate form loosely confined which may be used in carrying out the invention, and

FIGURES 2 and 3 show different types of porous anode assemblies which may be used in the cell shown in FIGURE 1 when a solid mass type porous anode is used.

The electrolytic cell diagrammatically shown in FIGURE 1 comprises a metal tank 1 having a cover plate 2 and an electrical non-conducting cylindrical liner 3 in which the electrolyte 4 is placed, and a carbon lead 5 extending part way into the tank through an opening in cover plate 2. As shown, cover plate 2 is fastened to tank 1 by means of a multiplicity of screws 6 to form a gas tight seal. Clamps or other means may be used. A pipe 7 is inserted in an opening 8 in cover plate 2 and provides a passageway through which the anode gas produced as a product inside of tank 1 may be withdrawn from the tank. The attachment of pipe 7 to cover plate 2 is gas tight and may be obtained by welding the outer periphery of the pipe to the cover plate or by having the end which is inserted in the cover plate threaded and the opening 8 also threaded to receive the pipe. Where the carbon lead 5 passes through cover plate 2 an electrical insulating seal 9 is used so that the gas tight seal is obtained. An electrical lead 10 through which the current

is supplied to the cell is attached to the carbon lead at the end which is not inserted into the tank. Another lead 11 is electrically connected to the surface of the tank which through a molten cathode 12 at the bottom of the tank completes the circuit for the current flow through the electrolytic cell. A molten cathode of an inert metal, such as lead, heavier than the electrolyte is generally used where the metal to be deposited at the cathode is lighter than the electrolyte. This simplifies the cell construction, since no provisions have to be made to entrap or remove the metal deposited from the surface of the electrolyte. Carbonaceous material 13 in particulate form which being lighter than the molten electrolyte floats on the surface surrounding and in contact with carbon lead 5. Carbon lead 5 is not immersed in the electrolyte itself.

In the operation of the cell, the cell is heated to the desired temperature. When the desired temperature is obtained an electrical potential is applied to leads 10 and 11 to provide a current flow through the electrolyte. The anode product which is substantially all gaseous is drawn from within the tank through pipe 7 after which it is further processed by known methods to recover and separate the fluorocarbon nitriles obtained from the other constituents. The metal depositing out from the electrolyte is deposited in the molten cathode and later recovered by known methods.

FIGURES 2 and 3 illustrate a porous anode assembly wherein a solid mass type of a porous anode is used. As shown in FIGURE 2 the anode assembly comprises a cylindrical carbon or graphite anode holder 20 having a passageway 21 extending through the center along its longitudinal axis. A hollow-cup shaped piece of porous carbon 22 is attached to the lower end of holder 20 with passageway 21 communicating with a hollow inside area 23 of the porous cup 22. At the upper end of holder 20, a pipe 24 is inserted in passageway 21 and thus provides a means by which the anode product forming at the porous cup may be removed from the cell. A lead 25 is attached to holder 21 and thus supplies the current to the anode and provides a means for completing the circuit in the cell.

FIGURE 3 shows a modification of the porous anode assembly shown in FIGURE 2. It comprises a carbon or graphite carbon holder 30 which at its lower end 31 is enlarged. The holder has a passageway 32 extending along its longitudinal axis which becomes enlarged at the lower end. The porous anode 33 in the shape of a plug is inserted in the lower end of the anode holder 30 in the enlarged area of the passageway. A pipe 34 is inserted in passageway 32 at the upper end of the anode holder. In the operation of the cell the porous anode portion of the anode assembly as shown in FIGURES 2 and 3 are immersed in the electrolyte.

The shape of the porous carbon anode used is immaterial. The hollow-cup type as shown in FIGURE 2 or the plug type as shown in FIGURE 3 are preferred especially where higher molecular weight fluorocarbons or fluorocarbon nitriles may be obtained. These compounds may be readily drawn through the porous anode and removed from the system through the passageway in the holder. Instead of using a hollow-cup type porous anode as shown in FIGURE 2 or a plug as shown in FIGURE 3 a solid cylindrical piece of the porous carbon material may be used as an anode. It may be necessary in some cases to use a hood or shield to enclose the solid anode to entrap the anode gases as they are formed and released in order to remove them from the system. Other types of anode assemblies which are apparent to those skilled in the art may also be used.

Illustrative examples of the alkali metal, alkaline earth metal, and earth metal fluorides which may be used as the fluoride constituent of the electrolyte are magnesium fluoride, aluminum fluoride, sodium fluoride, barium fluoride, strontium fluoride, calcium fluoride, lithium fluoride, and cesium fluoride. These metal fluorides are

non-volatile and stable at electrolysis temperature. Generally in the electrolysis, the anode product obtained will contain the same compounds regardless of the particular metal fluoride used as the fluoride constituent of the electrolyte. However, the ratio of the particular compounds obtained in the anode product may vary somewhat with the metal fluoride employed.

Although only one of the alkali metal fluorides alkaline earth metal fluorides, or earth metal fluorides may be used as the fluoride constituent of the electrolyte, a mixture of these metal fluorides is often used to increase the conductivity or lower the melting point of the bath. For this purpose, lithium fluoride is most commonly added to the other metal fluorides, but other mixtures and combinations may be used. When other fluorides are added to either increase conductivity or lower the melting point of a particular metal fluoride bath, the fluorides of metals which are higher in the electromotive series or more electronegative than the metal to be extracted at the cathode from the particular bath are preferred. By using fluorides of metals more electronegative, these metals will not deposit out at the cathode with the desired metal except at exceptionally high cathode current densities. Thus, the cathode product is not contaminated under normal operation conditions. Also in continuous operation of the cell, the metal fluoride added to the electrolyte is not depleted by the electrolysis and only the fluoride of the particular metal being deposited at the cathode has to be added continuously. For example, when lithium fluoride is added to a magnesium fluoride bath, the lithium is more electronegative than magnesium and thus will not deposit out at the cathode. Once the lithium fluoride is added to the bath it will not be depleted by the electrolysis and only magnesium fluoride has to be added for continuous operation.

Illustrative examples of the metal fluoride mixtures that may be used and the metal preferentially deposited out at the cathode are shown in the table below.

Fluoride Mixture	Metal Preferentially Deposited at the Cathode
NaF-LiF	Na
MgF ₂ -LiF	Mg
BaF ₂ -LiF	Li
AlF ₃ -LiF	Al
AlF ₃ -NaF	Al
AlF ₃ -NaF-LiF	Al
AlF ₃ -CaF ₂ -MgF ₂	Al
MgF ₂ -LiF-NaF	Na
MgF ₂ -LiF-CaF ₂	Mg
MgF ₂ -NaF	Na
MgF ₂ -CaF ₂	Mg
AlF ₃ -LiF-MgF ₂	Al
YF ₃ -LiF	Y

To the metal fluoride or fluoride mixture a metal cyanide or thiocyanate salt which is non-volatile and stable at the electrolysis temperature is added. By the electrolysis of the resulting electrolyte consisting essentially of the metal fluoride or metal fluorides and the metal cyanide or thiocyanate, fluorocarbon nitriles are obtained. It is preferred to add the metal salt of the same metal as that of the fluoride constituent of the electrolyte which is being deposited at the cathode in the bath. Thus, the cell can be continuously operated by just adding the metal fluoride electrolyte and the particular cyanide or thiocyanate. A non-volatile and stable cyanide or thiocyanide of the same metals as the alkali metals, alkaline earth metals, or earth metals of the fluoride which may be used other than the particular metal utilized in the bath may also be used. However, the metal of the cyanide or thiocyanide may continuously increase in the cell, if it is higher in the electromotive series, or deposit out at the cathode with the desired metal of the bath, if lower. In special cases, non-volatile and stable salts of metals other than those of the fluorides which may be used in the electrolyte may also be used, such as cuprous

thiocyanate. Most of these other metals are lower on the series and will deposit out at the cathode in conjunction with the electrolyte metal.

The concentration of metal salt added to the fluoride bath may vary with the particular salt used. The energy required for the production of the fluorine-containing compound is generally higher than for the production of compounds containing other anions. Consequently, a higher concentration of the fluoride in the bath is generally maintained to obtain a greater formation of the fluorine-containing compounds and thus minimize the formation of other compounds. Generally, an electrochemical equivalent ratio of the fluoride anion to the cyanide or thiocyanate anion in the range of 10:1 to 40:1 is used. It is preferred to have ratio of the fluoride to the other anions in the range of 15:1 to 30:1.

While an anode product containing a higher percentage of fluorocarbon nitriles is normally obtained at lower temperatures, an electrolysis temperature in the range of 700° to 1000° C. is generally used. The optimum of the temperature for a particular electrolyte may vary somewhat. The minimum temperature that may be employed is the melting point of the electrolyte used, since the electrolyte must be in the molten state. The maximum temperature is either limited by cell structure, the stability and volatility of the particular electrolyte employed or metal salt added to the bath, or the thermal stability of the particular fluorocarbon nitrile desired at the anode. Since at a lower temperature the construction of the cell is simplified, a temperature in the range of 700° to 1000° C. is thus generally preferred within which range an anode product containing a high percentage of fluorocarbon nitriles is obtained. However, for an electrolyte containing a $\text{LiF} \cdot \text{NaF} \cdot \text{AlF}_3$ mixture as the fluoride constituent, the optimum temperature is somewhat lower being in the range of 650° to 800° C.

Although anode current density below 1 and up to 100 amperes per square inch may be used with certain porous anodes, an anode density in the range of 1 to 40 amperes is generally employed, preferably in the range of 1 to 10 amperes per square inch. Generally, at a higher anode current density, the anode product contains a higher percentage of fluorocarbon nitriles. With an anode of carbonaceous material in particulate form loosely confined, an anode current density of over 5 amperes per square inch is seldom used due to the high voltage required. The cathode current density is generally in the range of 1 to 30 amperes per square inch. To obtain the current densities desired a voltage up to 30 volts may be employed, but a voltage in the range of 4 to 10 is preferred. For the loosely confined anode, a higher voltage may be required to obtain the desired anode current density.

Various electrolytic cell construction and various types of anodes which are apparent to those skilled in the art may be used. The particular anode adopted will generally depend upon the metal being deposited in the cell.

The term "earth metals," as used herein, means the elements aluminum, scandium, yttrium and lanthanum of the third group of the periodic system.

The term "stable," as used herein in reference to the metal fluoride and the metal cyanide or thiocyanate, means salts which are thermally stable and will not decompose due to temperature itself.

The term "non-volatile" as used herein in reference to the metal fluoride and the metal cyanide and thiocyanate means salts which do not have a vapor pressure in excess of 20 mm. of Hg at the electrolysis temperature.

The following examples further illustrate the invention but are not to be construed as limiting it thereto.

Example I

An electrolytic cell was employed in the preparation of fluorocarbon nitriles. The cell comprised a steel crucible with an alumina liner and was similar to that shown in FIGURE 1 except that a porous anode assembly similar

to that shown in FIGURE 3 was used instead of the particulate carbonaceous material.

To the cell, approximately 1,000 gm. of a mixture containing 30 weight percent of calcium fluoride, 35 weight percent of lithium fluoride, and 35 weight percent of magnesium fluoride were added. The contents were heated to 850° C. at which temperature the fluoride electrolyte was molten. Lead in the amount of 550 gm. was added to serve as a liquid cathode. The anode was a plug-type piece of porous carbon shaped as a truncated cone having diameters of 1 inch and $\frac{3}{4}$ inch and a height of 1 inch. The permeability of the porous anode as per the manufacturer's specifications was 4. The porous carbon anode was attached to a one inch diameter graphite rod which had a $\frac{1}{4}$ inch diameter hole through the center enlarged at one end to receive the porous anode.

Sodium cyanide in the amount of 60 gm. was added to the electrolyte and the cell was operated at a voltage of 7.8 volts with a current flow of 30 amperes. The spacing between the cathode and the anode was about $1\frac{1}{2}$ inches.

The anode gases produced were sampled by use of a gas bomb and analyzed by infra-red. The analysis of the gas is given below in mole percent.

Component:	Percent
CF_3CN -----	24.0
$(\text{CN})_2$ -----	32.5
CF_4 -----	11.0
C_2F_6 -----	3.7

In a manner similar to above, approximately the same yields of fluorocarbon nitriles are obtained when potassium cyanide, or other non-volatile and stable cyanides are used instead of sodium cyanide and when the electrolyte is $\text{MgF}_2 \cdot \text{LiF}$, $\text{CaF}_2 \cdot \text{LiF}$, $\text{NaF} \cdot \text{LiF}$, and $\text{NaF} \cdot \text{LiF} \cdot \text{CaF}_2$.

Example II

An electrolytic cell similar to that described in Example I was used for the electrolysis of a fluoride electrolyte to which a relatively small amount of sodium thiocyanate was added.

To the cell, approximately 1200 gm. of an electrolyte containing 48 weight percent of lithium fluoride and 52 weight percent of sodium fluoride were added. After the electrolyte was heated to 725° C., 500 gm. of lead were added to serve as a cathode. The cell was operated at a current of 25 amperes and 7 volts. During the operation of the cell, sodium thiocyanate was added at a rate of 8 gm. per hour.

An infra-red analysis of the anode gas indicated that the gas contained 17 mole percent of OF_3CN and a small amount of SF_4 .

What is claimed is:

1. A process for the preparation of a fluorocarbon nitrile, which comprises passing an electric current at a sufficiently low voltage to prevent anode effect through an electrolyte between a porous carbon anode and an insoluble cathode at a temperature sufficient to melt the electrolyte to obtain an anode product containing a fluorocarbon nitrile, said electrolyte consisting essentially of at least one metal fluoride which is non-volatile and stable at the electrolysis temperature selected from the group consisting of alkali metal fluorides, alkaline earth metal fluorides, and earth metal fluorides and a metal salt which is non-volatile and stable at the electrolysis temperature selected from the group consisting of metal cyanides and metal thiocyanates, and recovering the fluorocarbon nitrile from the anode product.

2. A process for the preparation of a fluorocarbon nitrile, which comprises passing an electric current at a sufficiently low voltage to prevent anode effect through an electrolyte between a porous carbon anode and an insoluble cathode at a temperature sufficient to melt the electrolyte to obtain an anode product containing a fluorocarbon nitrile, said electrolyte consisting essentially

of at least one metal fluoride which is non-volatile and stable at the electrolysis temperature selected from the group consisting of alkali metal fluorides, alkaline earth metal fluorides, and earth metal fluorides and a metal salt which is non-volatile and stable at the electrolysis temperature selected from the group consisting of metal cyanides, and metal thiocyanates in an amount such that the electrochemical equivalent ratio of the fluoride anions to the anion of the salt in the electrolyte is in the range of 10:1 to 40:1, and recovering the fluorocarbon nitrile from the anode product.

3. A process according to claim 2 wherein the electrolyte consists essentially of at least one alkali metal fluoride which is non-volatile and stable at electrolysis temperature and a metal cyanide which is non-volatile and stable at electrolysis temperature.

4. A process according to claim 2 wherein the electrolyte consists essentially of at least one alkaline earth metal fluoride which is non-volatile and stable at electrolysis temperature and a metal cyanide which is non-volatile and stable at electrolysis temperature.

5. A process according to claim 2 wherein the electrolyte consists essentially of at least one earth metal fluoride which is non-volatile and stable at electrolysis temperature and a metal cyanide which is non-volatile and stable at electrolysis temperature.

6. A process according to claim 2 wherein the electrolyte consists essentially of at least one alkali metal fluoride which is non-volatile and stable at electrolysis temperature and a metal thiocyanate which is non-volatile and stable at electrolysis temperature.

7. A process according to claim 2 wherein the metal fluoride is a mixture of at least one alkali metal fluoride and at least one alkaline earth metal fluoride and the metal salt is a metal cyanide.

8. A process for the preparation of a fluorocarbon nitrile, which comprises passing a current at a voltage up to 30 volts through an electrolyte between a porous carbon anode and an insoluble cathode at a temperature sufficient to melt the electrolyte to obtain a product at the anode containing a fluorocarbon nitrile, said electrolyte consisting essentially of a mixture of magnesium fluoride, lithium fluoride, and a metal cyanide which is non-volatile and stable at the electrolyte temperature in an amount such that the electrochemical equivalent ratio of fluoride to cyanide in the electrolyte is in the range of 10:1 to 40:1, and recovering the fluorocarbon nitrile from the anode product.

9. A process according to claim 8 wherein the metal cyanide is sodium cyanide, the electrochemical equivalent ratio of fluoride to cyanide in the electrolyte is in the range of 15:1 to 30:1, and the porous carbon anode is an intimately combined solid mass having a permeability of at least 0.2.

10. A process according to claim 9 wherein the porous carbon anode is an intimately combined solid mass having a permeability in the range of 4 to 20 and the electrolyte is at a temperature in the range of 700° to 1000° C.

11. A process for the preparation of a fluorocarbon nitrile, which comprises passing a current at a voltage up to 30 volts through an electrolyte between a porous carbon anode and an insoluble cathode at a temperature sufficient to melt the electrolyte to obtain a product at the anode containing a fluorocarbon nitrile, said electrolyte consisting essentially of a mixture of sodium fluoride, lithium fluoride, and a metal thiocyanate which is non-volatile and stable at the electrolyte temperature in an amount such that the electrochemical equivalent ratio of fluoride to thiocyanate in the electrolyte is in the range of 10:1 to 40:1, and recovering the fluorocarbon nitrile from the anode product.

12. A process according to claim 11 wherein the metal thiocyanate is sodium thiocyanate, the electrochemical equivalent ratio of fluoride to thiocyanate in the electrolyte is in the range of 15:1 to 30:1, and the porous carbon anode is an intimately combined solid mass having a permeability of at least 0.2.

13. A process according to claim 12 wherein the porous carbon anode is an intimately combined solid mass having a permeability in the range of 4 to 20 and the electrolyte is at a temperature in the range of 700° to 1000° C.

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