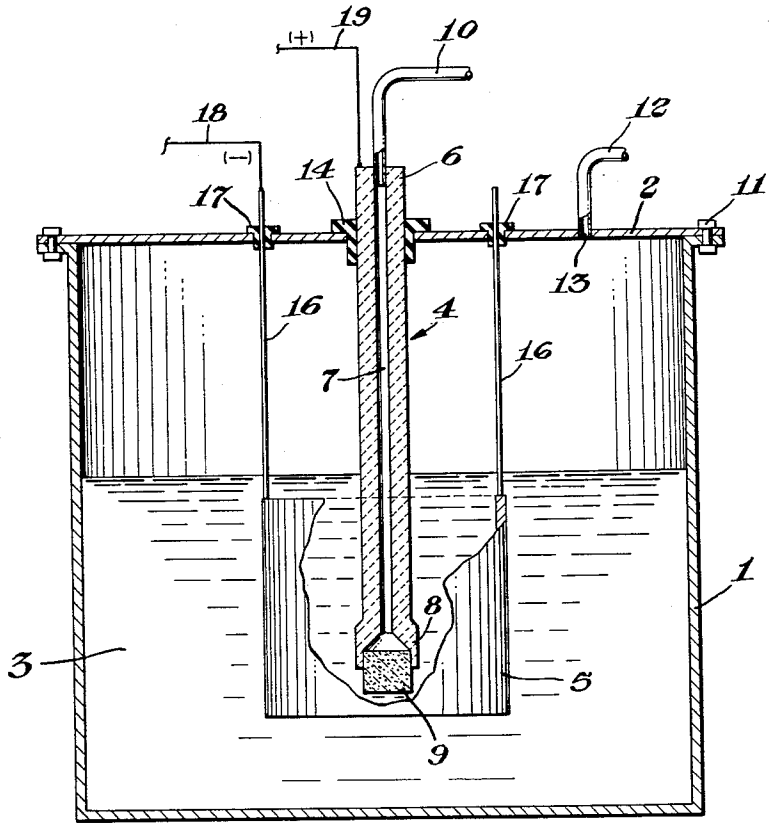
Feb. 20, 1962 F. OLSTOWSKI 3,022,233

PREPARATION OF SILICON

Filed Nov. 18, 1959



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United States Patent Office 3,022,233 Patented Feb. 20, 1962

3,022,233

PREPARATION OF SILICON

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Filed Nov. 18, 1959, Ser. No. 853,778
9 Claims. (Cl. 204—60)

This invention relates to a process for the preparation of silicon, and more particularly to the preparation of silicon and a metal silicide by electrolysis of a metal silicofluoride electrolyte.

Presently the preparation of silicon is mainly limited to the reduction of silica with a reducing agent at high temperatures in a thermoelectric furnace. A process whereby silicon and a metal silicide may be obtained by electrolysis of a metal silicofluoride would provide a convenient and economical method for the production of silicon and metal silicides.

It is therefore among the objects of this invention to provide a process for the preparation of silicon by electrolysis of a metal silicofluoride. A further object is to provide a method for the preparation of a metal silicide by electrolysis. And still a further object is to provide a method for the production of fluorocarbons by the electrolysis of metal fluoride to which a metal silicofluoride is added.

The above and other objects are attained according to the invention by passing an electric current through a molten electrolyte between a porous anode and an insoluble metal cathode to obtain a silicide of the cathode metal or the silicon. The electrolyte, non-wetting in respect to the anode, consists 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 to which is added at least one metal silicofluoride selected from the group consisting of alkali metal silicofluorides and alkaline earth metal silicofluorides.

It has been discovered that when a porous carbon anode is used in the electrolysis of an electrolyte consisting essentially of the particular silicofluorides and the particular metal fluoride or fluorides, silicon or a metal silicide of the cathode metal may be obtained at the cathode. An anode product obtained will contain a number of fluorine-containing compounds including both saturated and unsaturated fluorocarbons and also silicon-fluoride compounds, such as silicon tetrafluoride. The major portion of the anode product contains fluorine-compounds which are normally gaseous at room temperature, but higher molecular weight compounds which are oils at room temperature may also be obtained. With a porous carbon anode, the silicon or the silicide of the cathode metal are obtained by the electrolysis of the electrolyte without encountering "anode effect" which heretofore made the electrolysis of the above metal salts impractical.

The invention may be more easily understood when the detailed discussion is considered in conjunction with the drawing in which an electrolytic cell which may be used in carrying out the invention is diagrammatically illustrated.

The electrolytic cell shown in the drawing comprises a metal tank 1 having a cover plate 2 in which the electrolyte 3 is placed, a carbon porous anode assembly generally indicated as number 4 extending through an opening in cover plate 2 into the electrolyte 3 in the tank, and a cylindrical shell cathode 5 immersed in the electrolyte surrounding the porous anode at a distance.

The porous carbon anode assembly comprises a cylindrical carbon or graphite anode holder 6 having a passageway 7 extending through the center along its longitudinal axis. Passageway 7 at the bottom 8 of the holder is enlarged. A porous carbon plug 9 is inserted in the enlarged portion of passageway 7 and thus forms a porous anode. At the upper end of holder 6, a pipe 10 is inserted in passageway 7 and thus provides a means by which the anode product formed at the porous cup may be removed from the cell.

As shown, cover plate 2 is fastened to tank 1 by means of a multiplicity of bolts 11 to form a gas tight seal. Clamps or other means may also be used. A pipe 12 is inserted in an opening 13 in cover plate 2 and provides a passageway through which the anode gas which is not removed through the porous anode may be withdrawn from the inside of the tank. The attachment of pipe 12 to cover plate 2 is gas tight and may be obtained as 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 13 also threaded to receive the pipe. Where the holder 6 passes through cover plate 2, an electrical insulating seal 14 is used so that the gas tight seal is obtained.

Cathode 5 is a cylindrical shell inserted in the electrolyte 3 surrounding the porous anode 9. Rods 16 attached to the cylindrical shell extend through cover plate 2 and act to hold the cathode at the desired position. The rods are electrically insulated from the cover plate by seals 17 through which the rods pass. The sliding fit of the rods in seals 17 is sufficiently tight so that the cathode may be adjusted to be immersed in the electrolyte at the desired level by just sliding the rods through the seals. The cathode is electrically connected to lead 18 through one of the rods. Another electrical lead 19 through which the current is supplied to the cell is attached to holder 6 at the upper end which completes the circuit for the current flow through the electrolytic cell.

A mixture of the metal silicofluoride and metal fluoride of various concentrations may be used as the electrolyte. Generally, the metal silicofluoride is a substantial constituent of the electrolyte, e.g. 10 to 35 weight percent, although as low as about 2 weight percent would be operative. Concentration of the metal silicofluoride in the range of 10 to 20 weight percent is preferred. However, with many of the silicofluorides a high concentration of the silicofluoride may not be maintained in the electrolyte without using higher pressures due to the decomposition and vaporization of the silicofluoride at the electrolysis temperature. Since the metal silicofluoride may be dissolved or may form complex compositions with the metal fluoride or the fluorides used in the electrolyte, the maximum amounts of the silicofluoride which may be retained in the electrolyte without excessive loss from decomposition and vaporization at atmospheric pressure depends upon the metal fluoride or fluorides used in the electrolyte, for example, an electrolyte containing potassium fluoride can retain a higher concentration of a metal silicofluoride than sodium fluoride. To maintain the desired concentration of the metal silicofluoride in the electrolyte, the metal silicofluoride may be continuously added to the electrolyte to offset the silicofluoride lost by decomposition and vaporization. Also, the metal silicofluoride may be formed in situ in the electrolyte by addition of silicon tetrafluoride to react the silicon tetrafluoride with the metal fluoride making up the electrolyte to form the metal silicofluoride. Thus, silicofluorides of alkali metals, alkaline earth metals, and earth meals which are non-wetting with respect to the anode may be used as the silicofluoride constituent of the electrolyte. Most of the silicofluorides are sufficiently non-volatile and when dissolved in the metal fluoride used as the electrolyte at the

electrolysis temperature to be retained in an amount of at least 2 weight percent without having to employ a superatmospheric pressure. Illustrative examples of these salts are lithium silicofluoride, magnesium silicofluoride, calcium silicofluoride, barium silicofluoride, sodium silicofluoride, and potassium silicofluoride.

Representative examples of alkali metal, alkaline earth metal, and earth metal fluorides which may be used as the fluoride constituent in 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 and are also non-wetting with respect to the anode. Normally potassium fluoride wets the anode and may not be used in large amounts in the electrolyte without encountering anode effect. However, in the presence of a silicofluoride metal salt, even in minor amounts, the mixture generally becomes non-wetting an may be used.

Although only one of the alkaline metal fluorides, alkaline earth metal fluorides, or earth metal fluorides may be used as a fluoride constituent in 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. Examples of some of the metal fluoride mixtures that may be employed are NaF·LiF,

MgF_2·LiF, BaF_2·LiF, AlF_3·LiF, AlF_3·NaF·LiF, AlF_2·CaF_2·MgF_2, MgF_2·LiF·NaF, MgF·LiF·CaF_2, MgF_2·NaF, MgF_2·CaF_2, and AlF_3·LiF·MgF_2

The porous anode used in the electrolysis may be an intimately combined solid cohered mass as shown as number 9 in the drawing which is made by combining an 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 loosely confined. A porous anode which is intimately combined by sintering to form a solid cohered mass is generally preferred.

A solid mass type porous anode having a permeability of at least 1 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 1 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 permeability generally used in the range of 1 to 40, normally all practical anode current densities may be used without encountering this objectional 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.

The shape of the porous carbon anode used is immaterial. A plug type porous anode assembly as shown in the drawing is preferred especially where higher molecular weight fluorocarbons 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 the plug, a hollow-cup type porous anode to fit over bottom end of the holder or a one piece cylindrical piece of porous carbon material may be used. It may be necessary in some cases to use a hood or shield to enclose the one piece 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.

"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 inch thickness at a pressure differential of two inches of water. The term "porous," as used herein means gas permeable.

While the current efficiency and the yields of higher molecular weight fluorocarbons in the anode product 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 material which are operative. Due to its availability petroleum coke in particulate form is preferred. Generally particles of the carbonaceous material larger than 1 inch are not used except in a large unit where a large bed is employed. Particles as small as those passing through a 100 standard mesh screen and being retained on a 300 mesh screen are operative. However it is preferred to use carbonaceous material which will pass through a number 6 standard screen and be retained on a number 40.

When the carbonaceous material is used as an anode, a cell similar to that shown in the drawing may be used. The porous anode assembly which is indicated generally by number **4** is removed and in its place a similar holder is inserted which has the lower end enlarged to a greater extent than that shown in the drawing in which the carbon in particulate form is placed.

In the operation of the cell as shown in the drawing, the electrolyte is placed in the cell and the cell is heated to melt the electrolyte. The cover plate with the porous anode and cathode assemblies is placed on the tank and the anode and cathode assemblies are adjusted so that when the cover plate is tightened on the tank the porous plug anode at the lower end of the holder and the cathode are immersed in the electrolyte. After the cover plate is tightened the cell is heated again until the desired temperature is obtained. When the desired temperature is obtained, an electrical potential is applied to leads **18** and **19** to provide a current flow through the electrolyte. The anode product which may be substantially all gas is drawn from the cell through pipes **10** and **12** after which it is further processed by known methods to recover and separate the products obtained. The anode product may contain some silicon tetrafluoride which is one of the constituents usually obtained upon decomposition of the metal sillicofluoride. At the electrolysis temperature decomposition of the metal silicofluoride to some extent is generally obtained.

The silicon is deposited upon the cathode and generally reacts with the cathode to form a silicide. After sufficient amount of the silicide is formed to cover the portion of the cathode immersed in the electrolyte, silicon is then deposited out. Thus, when it is desirable to obtain a metal silicide of iron, copper, cobalt, chromium, zirconium, nickel and metals which have melting points above the electrolysis temperature and form silicides, the metal is used as the cathode in the cell.

It is not necessary to use a solid cathode as shown in the drawing. After known suitable modifications to the cell are made, molten metal cathodes may also be used in the cell. When a molten metal, such as lead, zinc, and cadmium, which do not form silicides is used as a cathode, a portion of the silicon may be deposited in the molten metal. However, a large percentage of it is generally dispersed throughout the electrolyte in minute particle size.

While the maximum electrolysis temperature may be limited either by the cell construction or the stability

and volatility of the particular electrolyte employed, a temperature in the range of 450° to 800° C. is generally used. At temperatures above 800° C. a larger portion of the silicofluoride values is converted to silicon tetrafluoride. The minimum temperature that may be employed is the melting point of the electrolyte, but at temperatures this low, the power efficiency may be considerably decreased. Higher voltages are required to obtain the desired current flow through the cell.

The cathode employed in the cell has sufficient cross sectional area so that in the operation of the cell a cathode current density in the range of 0.1 to 30 amperes per square inch is obtained. A cathode current density in the range of 0.5 to 5 amperes is preferred. The amount of other metals of the electrolyte besides silicon which are deposited at the cathode may increase with an increase in the cathode current density. Thus relatively low densities are required to minimize the contamination of the silicon with the other metals.

The anode current density affects the composition of the anode product obtained. Generally at a higher anode current density the anode product contains a higher percentage of high molecular weight fluorocarbons, while at low current densities carbon tetrafluoride may be one of the main constituents. While an anode current density in the range of 0.5 to 40 amperes is generally employed, the preferred range is 1 to 10 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 20 volts is generally used.

Various electrolytic cell construction and various types of anodes and cathodes apparent to those skilled in the art may be used.

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

The term "stable," as used herein in reference to the metal fluorides, 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, means salts which do not have a vapor pressure in excess of 20 millimeters of mercury at the electrolysis temperature.

The invention is further illustrated by the following examples but is not to be construed as limited thereto.

Example I

An electrolytic cell similar to that shown in the drawing was used in the electrolysis of an electrolyte consisting essentially of 45 weight percent lithium fluoride, 35 weight percent sodium fluoride, and 20 weight percent sodium silicofluoride. The cell was constructed of a 4" I.D. nickel tank. The cathode was a 2¼" I.D. x 4" cylindrical shell of copper. The anode assembly was similar to that shown in the drawing. The porous carbon plug was 1" in diameter and 2" long. It had a permeability of 4, as per manufacturer's specifications.

The cell was heated to about 630° C. to melt the electrolyte and the cover was bolted down so that the anode and cathode were immersed in the electrolyte. The electrolyte was maintained at 630° C. and approximately 20 amperes of current was passed through the cell for a total of 2 hours. To obtain this current flow, a potential of 20 volts was used. This gave a cathode current density of approximately 0.6 ampere per square inch and an anode current density of 3.5 amperes per square inch.

Gases produced at the anode were withdrawn from the inside of the anode and the inside of the tank through lines comparative to lines **10** and **12**, respectively, in the attached drawing. The anode gases were collected in glass bombs by displacement of the air. Approximately 3 times as much product was obtained from the inside of the anode as from the tank. Upon analysis by infrared technique they were found to contain the following in mole percent:

Component	Inside Anode	Inside Tank
CF_4	24.0	21.5
C_2F_6	25.0	8.4
C_3F_8	7.5	1.2
SiF_4	15	57.0
CO_2	3.5	2.9

Upon dismantling the cell a sludge-like deposit was found adhering to the cathode, the sodium fluoride, lithium fluoride, and sodium silicofluoride were leached from the deposit by washing with hot water and with cold aqueous HCl and then boiled in concentrated HCl. Three grams of amorphous silicon were obtained. The copper cathode surface had a silver bronze cast which was determined by X-ray methods to be copper silicide (γ-Cu_5Si).

Example II

The cell of Example I was operated with the same electrolyte except that a cathode of mild steel was used. The electrolyte was maintained at 640° C. and at a cell potential of 15 volts, 25 amperes were passed through the cell for a total of 2.4 hours.

The anode gases obtained from the inside of the anode and inside of the tank were in a ratio of 3:1 which was about the same ratio obtained in Example I. Upon infrared analysis the gases were found to contain the following in mole percent:

Component	Inside Anode	Inside Tank
CF_4	8.6	26.0
C_2F_6	5.3	22.0
C_3F_8	2.4	
CO_2	6	3.5
SiF_4	52.0	3.5

The sludge-like deposit adhereing to the cathode was found to contain 1.7 grams of amorphous silicon after the electrolyte was removed by leaching with hot water and with cold aqueous HCl and then boiled in concentrated HCl.

Similar results were obtained with an electrolyte containing 33% K_2SiF_6, 33% LiF, and 33.4% NaF and using a molten lead cathode. The sludge-like deposit was obtained upon the lead cathode.

What is claimed is:

1. A process for the preparation of silicon which comprises passing an electric current through an electrolyte between a porous carbon anode and an insoluble cathode at a temperature sufficient to melt the electrolyte to obtian a cathode product, said electrolyte being non-wetting with respect to the anode consisting essentially of at least one metal fluoride which is non-volatile and stable at electrolysis temperature selected from the group consisting of alkali metal fluorides, alkaline earth metal fluorides, and earth metal fluorides to which is added at least one metal silicofluoride selected from the group consisting of alkali metal silicofluorides and alkaline earth metal silicofluorides in an amount of at least 2.0 weight percent.

2. A process for the preparation of silicon which comprises passing an electric current at a cell potential of less than 30 volts through an electrolyte between a porous carbon anode and an insoluble metal cathode at a temperature in the range of 450° to 800° C. and sufficient to melt the electrolyte to electrolyze the electrolyte to produce the silicon at the cathode and a fluorine-containing product at the anode, said electrolyte being non-wetting with respect to the anode consisting essentially of at least one metal fluoride which is non-volatile and stable at electrolysis temperature selected from the group consisting of alkali metal fluorides, alkaline earth metal fluorides, and earth metal fluorides to which is added at least

one metal silicofluoride selected from the group consisting of alkali metal silicofluorides and alkaline earth metal silicofluorides in an amount at least 2 weight percent.

3. A process according to claim 2 wherein the porous anode is an intimately combined solid mass having a permeability of at least 0.2.

4. A process according to claim 3 wherein the electrolyte consists essentially of at least one alkali metal fluoride to which is added at least one alkali metal silicofluoride.

5. A process for the preparation of silicon which comprises passing an electric current at a cell potential of less than 30 volts between a porous carbon anode and an insoluble metal cathode at a temperature in the range of 450° to 800° C. to electrolyze the electrolyte to produce silicon at the cathode and a fluorine-containing product at the anode, said electrolyte consisting essentially of a mixture of sodium fluoride and lithium fluoride to which is added sodium silicofluoride in an amount of at least 2 weight percent.

6. A process according to claim 5 wherein the porous anode is an intimately combined solid mass having a permeability of at least 0.2.

7. A process according to claim 5 wherein the sodium silicofluoride is added to the sodium fluoride-lithium fluoride mixture in an amount of from 10 to 20 weight percent, the porous anode is an intimately combined solid mass having a permeability in the range of 4 to 20, and the cathode is copper.

8. A process for the preparation of silicon which comprises passing an electric current at a cell potential of less than 30 volts between a porous carbon anode and an iron cathode at a temperature in the range of 450° to 800° C. to electrolyze the electrolyte to produce silicon and metal silicide at the cathode and a fluorine-containing product at the anode, said electrolyte consisting essentially of a mixture of sodium fluoride and lithium fluoride to which is added potassium silicofluoride in an amount of at least 2 weight percent.

9. A process according to claim 8 wherein the potassium silicofluoride is added to the sodium fluoride-lithium fluoride mixture in an amount of from 10 to 20 weight percent, the porous anode is an intimately combined solid mass having a permeability in the range of 4 to 20, and the cathode is copper.

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