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" A PROCESS FOR THE PRODUCTION OF SOLID ION CONDUCTOR ARTICLES SUCH AS TUBES , DIAPHRAGMS AND THE LIKE AND ARTICLES OBTAINED THEREBY "

Council of Scientific & Industrial Research,
Rafi Marg, New Delhi - 110001, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

The following specification describes the nature of this invention.

PRICE: TWO RUPEES

1 5 2 4 7 6

This is an invention by Kuppuswamy Venugopalan, Scientist, Veeraraghava Aravamuthan, Scientist and Handady Venkatakrishna Udupa, Director, all of Central Electrochemical Research Institute, Karaikudi, 623006, Tamil Nadu, India.

The object of this invention is to find out a solid ion conductor which can selectively conduct sodium ion. A new product, namely, complex phosphate of zirconium-sodium-silicate has been worked out which has good electrical conduction at 350-360^{o}C for sodium ion.

The product is a complex phosphate compound of zirconium oxide, silica and sodium. The product is formed by reacting zirconium oxide (30-50%), sodium silicate (20-60%) or sodium carbonate (20-50%) and phosphate (20-60%) or either sodium or ammonium or both salts with sodium salts, ultimately to form complex phosphate compound of sodium oxide, zirconium oxide and silica.

The mixtures of the above oxides are suitably mixed and ball-milled for 12 to 24 hours and are heated to 100-200°C for 2 to 6 hours, again heated to 600-1000°C for 2 to 6 hours, again the same material is heated to 1100-1350°C for 6 to 10 hours. The resulted product is again ball-milled and sieved to 100-400 mesh. This product is isostatically pressed to get the desired size tubs. These tubes are fired at 100 to 1300°C in 6 hours.

EXAMPLE 1

A mixture of -

Sodium carbonate	:	96 g
Zirconium oxide	:	148 g
Silica	:	72 g
Ammonium phosphate	:	78 g

is ball-milled and heated to 100-200°C for 5 hours. Again the same material is heated to 950°C for 5 hours. Once more the same product is heated to 1200-1300°C for 6 hours, cooled and ball-milled. Sieved through 200 mesh. The powder is isostatically pressed to 15 cm length, 1.5 cm dia with wall thickness to 2-3 mm. This tube is again fired at 1200-1300°C for 6 hours. The non-porous tube is tested in sodium nitrate and nitrite electrolyte at 350°C. 5 mm stainless steel rod is dipped inside the tube, stainless steel tube of 300 mm diameter surrounds the tube. The resistance of 90 mm length of this tube gave a resistance of 1.3 ohms at 3 KHz between two elements dipped in the molten nitrate and nitrite mixture.

EXAMPLE 2

A mixture of

Sodium carbonate	:	96 g
Zirconium oxide	:	148 g
Silica	:	72 g
Ammonium phosphate	:	78 g

gave similar treatment as above.

The tube was immersed in a bath of molten zinc chloride, sodium chloride to a depth of 50 mm. Sodium metal was kept inside the ceramic tube with copper as lead. The tube was properly closed. A cylindrical graphite tube was kept inside zinc chloride sodium chloride melt. At 4 volts DC 2.1 A current pass through the tube either way at 360°C.

EXAMPLE 3

A mixture of -

Sodium carbonate	:	96 g
Zirconium chloride	:	148 g
Silica	:	72 g
Ammonium phosphate	:	78 g

was given the treatment similar to above, the tube was isostatically pressed, fired at 1200-1300°C. The tube was non-porous. The conductivity was measured using sodium metal inside the tube and zinc chloride sodium chloride outside the tube. Graphite tube was immersed in the bath surrounding the ceramic. The resistance between graphite and sodium metal was found to be 0.39 ohms for 50 mm height of the tube at 3 KHz.

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The advantages of the present invention are:

1) The solid electrolyte prepared by the process above has better electrical characteristics at the temperature range 200-350°C than beta alumina.

2) This solid electrolyte can be prepared much easier than that of beta alumina such as temperature of preparation, easy composition range and also easily amenable to fabrication of end products such as tubes.

3) This solid ion conductor can be used for (a) high energy density batteries such as sodium-sulphur or sodium-chlorine etc; (b) for the electrowinning of sodium metal at about 300°C compared to present method of 580-600°C. The product can also have high purity sodium compared to that in the existing processes.

Dated this 21st day of June, 1979.

S. Kumar

S. Kumar,
Asstt. Patents Officer
Council of Scientific & Industrial Research
III Floor, CSIR Complex.
NPL Campus. Libraryroad,
Pusa, New Delhi-110012.

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THE PATENTS ACT, 1970

COMPLETE SPECIFICATION

(Section—10)

" A PROCESS FOR THE PRODUCTION OF SOLID ION CONDUCTOR ARTICLES SUCH AS TUBES, DIAPHRAGMS AND THE LIKE AND ARTICLES OBTAINED THEREBY "

Council of Scientific & Industrial Research,
Rafi Marg, New Delhi - 110001, India, an Indian
registered body incorporated under the Registration
of Societies Act (Act XXI of 1860)

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

This is an invention by Kuppuswamy Venugopalan, Veeraraghava Aravamuthan and Handady Venkatakrishna Udupa, Scientists all of the Central Electrochemical Research Institute, Karaikudi-623006, India.

This invention relates to a process for the production of solid ion conductor articles and articles obtained thereby. The articles are such as tubes or diaphragm for use in-sodium metal recovery or for energy storage devices employing fused chlorides or sulphides or mixtures thereof.

According to hitherto known processes solid sodium ion conducting diaphragm have been developed. It comprises a compound of sodium oxide and aluminium doped with magnesia or lithia. The product is called beta-alumina. For its preparation, aluminium should be below sub-micron size particles. It is difficult to obtain pore-free silica articles. The article has to be fired at 1600-1700°C. To attain, control and measure this high temperature is not so easy. At this temperature, the volatilisation of sodium oxide is high and this disturbs the critical composition of beta-alumina.

The difficulties of heating the beta alumina above 1600°C has been overcome by process and articles that have been developed by this invention. The firing temperature of the green article is 1300°C. This temperature is easily attainable, controllable and measureable. At this temperature, the volatilisation of sodium oxide is negligible. The material is easily amenable to isostatic pressing which can be fired to a pore-free article.

The present invention consists of an article and method for the preparation of zirconium phospho-silicate which can be employed as a solid conducting diaphragm, which can easily conduct sodium ion alone similar to beta alumina. However, the new article is easily prepared by firing the final green tubes at 1300°C instead of 1600-1700°C as is the case with beta alumina.

The new solid electrolyte is prepared by firing the gree tube at 1300°C. The temperature can be easily attained, controlled and measured in a silicon carbide resistor furnace. The zirconium phosphosilicate powder also easily amenable to isostatic pressing than beta alumina. In the case of the beta alumina firing temperature is High 1600-1700°C and same is difficult to attain, control and measure.

This solid ion conductor can be used for (a) high energy density batteries such as sodium-sulphure or sodium-chlorine etc.,(b) for the electrowinning of sodium metal at about 300°C compared to present method of 580-600°C. The article can also have high purity sodium compared to that in the existing processes.

The articles which can be in the form of a tube or diaphragm is prepared by the present invention conducts sodium ions in the solid state at 300-350°C. So this article can be utilised for preparation of sodium metal at 300°C by using suitable molten electrolyte. It can be used as a diaphragm material for sodium-chlorine battery in which the sodium and chlorine are seperated by the solid diaphragm which conducts sodium ions through it. Similarly, the same can be used for sodium-sulphur battery which is a high energy density battery. This product also seperates the anodic and cathodic part of the battery, but it allows sodium ions alone to pass through from one chamber to another.

The article is formed of a complex phosphate compound of zirconium oxide, silica and sodium. The article is formed by reacting zirconium oxide (30-50%), sodium silicate (20-60%) and/or sodium carbonate (20-50%) and phosphate (20-60%) of either sodium and/or ammonium silicate, phosphate compositions of zirconium salts with sodium salts, ultimately to form complex phosphate compound of sodium oxide, zirconium oxide and silica.

Accordingly this invention provides a process for the production of solid ion conductor articles which comprises reacting zirconium oxide with sodium silicate or sodium carbonate and phosphates of sodium and/or ammonium or both at 1000-1350°C, grinding the reaction product and sieving to obtain a 100-400 mesh size product, isostatically pressing same to desired shape and firing the shaped article at 1000° to 1300°C over a period of upto 6 hours.

The mixtures of the above oxides are suitably mixed and ball-milled for 12 to 24 hours and are heated to 100-200°C for 2 to 6 hours, again heated to 500-1000°C for 2 to 6 hours, again the same material is heated to 1000-1350°C for 6 to 10 hours and the resulted product is again ball-milled and sieved to 100-400 mesh. This product is isostatically pressed to get the desired size tubes. These tubes are fired at temperatures 1000 to 1300°C in 6 hours slowly raising the temperature.

The present invention consists of an article which can be employed as a solid ion conductor to conduct only sodium ions through its walls which is non-porous to gases and electrolyte somewhat similar to beta alumina. But the present article can be easily and conveniently prepared than beta alumina.

The invention is for the illustrated by the examples below :-

EXAMPLE I

A mixture of -

Sodium carbonate	...	96	g
Zirconium oxide	...	148	g
Silica	...	72	g
Ammonium phosphate	...	78	g

is ball-milled and heated to 100-200° for 5 hours. Again the same material is heated to 950°C for 5 hours. Once more the same product is slowly heated to 1300°C from 100°C for 6 hours, cooled and ball-milled, Sieved through 200 mesh, the powder is isostatically pressed to 15 cm length. 1.5 cm dia. with wall thickness to 2-3 mm. This tube is again slowly heated to 1300°C from 100°C for hours. The non-porous tube is tested in sodium nitrate and nitrite electrolyte at 350°C. 5 mm stainless steel rod is dipped inside the tube, stainless steel tube of 300 mm dia surronds the tube. The resistance of 90 mm length of this tube gave a resistance of 1.3 ohms at 3 Khs between two elements dipped in the molten nitrate and nitrite mixture.

EXAMPLE II

A mixture of -

Sodium carbonate	...	96	g
Zirconium oxide	...	148	g
Silica	...	72	g
Ammonium phosphate	...	78	g

was given similar treatment as above.

The tube was immersed in a bath of molten zinc chloride, sodium chloride to a depth of 50 mm. Sodium metal was kept inside the ceramic tube with copper as lead. The tube was properly closed. A cylindrical graphite tube was kept inside zinc chloride sodium chloride melt. At 4 volts DC 2.1. A current was passed through th tube either way at 360^{o}C. After electrolysis, sodium metal was tested for zinc. No zinc was detected. This indicates, the solid electrolyte is selective to sodium.

EXAMPLE III

A mixture of -

Sodium carbonate	...	96	g
Zirconium chloride	...	148	g
Silica	...	72	g
Ammonium phosphate	...	78	g

was given the treatment similar as above, the tube was isostatically pressed, slowly heated to 1300°C from 100°C for six hours. The tube was non-porous. The conductivity was measured using sodium metal inside the tube and zinc chloride sodium chloride outside the tube. Graphite tube was immersed in the bath surrounding the ceramic. The resistance between graphite and sodium metal was found to be 0.39 ohms for 50 mm height of the tube at 3 KHz.

<u>WE CLAIM</u> :

1. A process for the production of solid-ion conductor articles such as tubes and diaphragms and the like comprising admixing silica and/or sodium carbonate with zirconium oxide and sodium or ammonium phosphates and subjecting the admixture to a the steps of heating at a temperature range of 1000° to 1350°C, grinding the reaction product to separate a 100-400 mesh size product isostatically pressing the same to obtain desired shaped articles and firing the same at 1000° to 1300°C for a period of upto 6 hours.

2. Process as claimed in claim 1 wherein the admixture is ball-milled for 12-24 hours and subjected to plurality of steps of heating first at a temperature range of 100°-200°C for a period of 26 hours, and then at 600°-1000°C for a period of 2-6 hours and further heated at 1000°-1350° for another period of 6 to 10 hours.

3. Process as claimed in claims 1 or 2 wherein the reaction

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product is further ball-milled to grind and separate a 100-400 mesh size product and subjecting the same to isostatically pressing to obtain the desired shaped articles in the form of tubes, diaphragms and the like.

4. Process as claimed in any of the preceding claims wherein the shaped articles formed are subjected to firing at a temperature range of 1000^{o}-$1300^{o}C$ for a time period of upto 6 hours.

5. Process as claimed in any of the preceding claims wherein 30-50% of zirconium oxide, 20-60 % of sodium silicate and/or 20-30% of sodium carbonate by wt. is admixed with 20-60% by wt. of sodium and/or ammonium phosphate for interaction.

6. Process for the production of solid ion conductor articles substantially as herein described and illustrated.

7. Solid ion conductor articles ~~in the form of~~ such as tubes, diaphragms and the like whenever produced by the process as described and illustrated herein.

Dated this 5th day of September 1980.

(I.M.S. MAMAK)
PATENTS OFFICER
COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH