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(54) **Sodium-resistant Glass**

(57) A sodium resistant sealing glass has an aluminoborate glass composition in which glass stability is improved by the incorporation of calcium oxide, strontium oxide and/or barium oxide. The glass comprises

10—30 weight percent alumina, 35—50 weight percent boron oxide, 15—40 weight percent of a mixture of calcium oxide, barium oxide and/or strontium oxide, 0—20 weight percent of silica, and 0—5 weight percent of sodium oxide, lithium oxide, and/or potassium oxide.

GB 2 035 995 A

SPECIFICATION

Sodium Resistant Sealing Glass

This invention relates generally to sodium resistant sealing glasses and, more particularly, to such glasses with an aluminoborate glass composition with specific modifying oxides.

Such sodium resistant sealing glasses are useful for sealing a ceramic ring or flange to a solid electrolyte tube in a sodium-sulfur battery. Such a sodium-sulfur battery employing a sealing glass in this manner is described in U.S. Patent 3,946,751-Breiter, et al, entitled "Cell Casing With a Hermetic Mechanical Seal and a Hermetically Sealed Sodium-Sulfur Cell".

The term solid electrolyte tube as used above in the discussion of a sodium-sulfur battery, includes ion-conductive materials such as beta-alumina, beta''-alumina, mixtures thereof and related compounds.

In the above mentioned U.S. Patent No. 3,946,751-Breiter, et al, a cell casing and a hermetically sealed sodium-sulfur cell are disclosed and claimed wherein the cell casing includes a hermetic mechanical seal joining two opposed outer metallic casing portions to an electrically insulating ceramic ring supporting an inner casing of a solid ion-conductive material. The hermetically sealed sodium-sulfur cell has the above type of casing with a sodium negative electrode in the inner casing end and a positive electrode of sulfur in conductive material in an outer casing portion surrounding the inner casing. A glass seal seals a portion of the outer wall of the inner casing of the solid sodium ion-conductive material adjacent its open end within and to the ceramic ring.

In U.S. Patent 4,132,820, there is described and claimed a composite body with a glass coating which has sodium resistance, low alkali ion-conductance and a thermal expansion of 7.3 to 6.1×10^{-6} inches/inch/ $^{\circ}\text{C}$. The glass coating compositions can be selected from the table set forth on page 6, the specific glass coatings set forth on page 7, or the table set forth on page 8 of the above-mentioned co-pending patent application. As opposed to the present invention, none of the glass coatings set forth in the above-identified copending application recite a combination of modifying oxides of calcium oxide, strontium oxide and barium oxide in a range of 15 to 40 weight percent of the glass composition.

The present invention provides a sodium resistant aluminoborate sealing glass comprising 10—30 weight percent alumina, 35—50 weight percent boron oxide, 15—40 weight percent of a mixture of alkali earth oxides of calcium oxide, barium oxide and strontium oxide, 0—20 weight percent of silica, and 0—5 weight percent of a mixture of alkali metal oxides of sodium oxide, lithium oxide, and potassium oxide.

Sodium-sulfur cells incorporate generally a sealing glass in the ceramic-to-ceramic seal between an electrically insulating flange and a solid ion-conductive electrolyte made generally of

beta or beta''-alumina. In most sodium-sulfur cell designs, the sealing glass is in contact with molten sodium from the sodium compartment of the sodium-sulfur cell and, therefore, it must offer adequate resistance against sodium attack.

Further, substantial changes in the sealing glass composition are liable to occur during the sealing of the flange to the electrolyte due to ionic interdiffusion between the glass and the ceramic component. This effect of change in glass composition is particularly serious at the glass-electrolyte interface. Our studies have indicated that such changes lead to glass devitrification and deleterious thermal expansion mismatches between sealed components with resulting seal failures and termination of cell operation.

We have found an improved sodium resistant sealing glass which offers good sodium resistance as well as stability against interfacial reactions and devitrification. Our sealing glass has been selected from aluminoborate compositions containing a specific combination of alkali earth oxides. Ceramographic examinations of seals and results of seal tests for extended cycling indicated the excellent behavior of our improved sodium resistant sealing glass. The unique properties of our sealing glass makes it suitable for other types of seals where sodium resistance is desired.

Previously, silicate and borosilicate glasses have been used as sealing glasses in sodium-sulfur cells. For example, in U.S. patent 4,037,027, there is described a borosilicate glass of the composition having 70.36% SiO_2 , 1.88% Al_2O_3 , 19.56% B_2O_3 and 8.20% Na_2O . As opposed to silicate and borosilicate glasses, we employ an aluminoborate sealing glass with a specific combination of modifying alkali earth oxides of calcium oxide, strontium oxide and barium oxide, with resulting glass stability. These aluminoborate glass compositions are more resistant to sodium attack than silicate or borosilicate glasses. Thus, our improved sodium resistant sealing glass provides good sodium resistance and excellent glass stability.

We found that we could form a sodium resistant aluminoborate sealing glass which comprises 10—30 weight percent alumina, 35—50 weight percent boron oxide, 15—40 weight percent of a mixture of alkali earth oxides of calcium oxide, barium oxide and strontium oxide, 0—20 weight percent of silica, and 0—5 weight percent of a mixture of alkali metal oxides of sodium oxide, lithium oxide, and potassium oxide. The resulting sealing glass had excellent sodium resistant properties and improved glass stability.

We found further that this sealing glass had a thermal expansion coefficient which matched closely that of both eta-aluminas and alpha-alumina, which are employed generally as the ion-conductive tube and the electrically insulating flange in a sodium-sulfur battery, respectively. We found two preferred sodium resistant aluminoborate sealing glasses within the composition range of our sealing glass. One sealing glass consisted of 19 weight percent

alumina, 45 weight percent boron oxide, 6 weight percent calcium oxide, 12 weight percent barium oxide, 10 weight percent strontium oxide, and 8 weight percent silica. The other sealing glass

5 consisted of 19 weight percent alumina, 45 weight percent boron oxide, 7 weight percent calcium oxide, 6 weight percent barium oxide, 13 weight percent strontium oxide, and 10 weight percent silica.

10 The sodium stability of our two preferred sealing glass compositions was clearly demonstrated in accelerated tests with virgin glasses. After 160 hours at 350°C in sodium vapor, both of our aluminoborate glass

15 compositions exhibited little, if any, discoloration. However, a high silica sealing glass consisting of 50 weight percent silica, 10 weight percent alumina, 30 weight percent barium oxide, and 10 weight percent boron oxide turned dark brown.

20 Discoloration effects, although qualitative, indicate the presence of metallic sodium in the glass and thus provide a measure of sodium permeability. Excess sodium migration within the sealing glass is generally accompanied by fracture

25 processes which, in the case of sodium-sulfur batteries, leads to cell failure.

A second significant property of our sodium resistant aluminoborate sealing glass is the stability of the glass and its resistance to devitrification. That is, the sealing glass must be able to withstand slight changes in composition without crystallizing. The temperatures involved in the sealing operation enable ionic diffusion and even some dissolution to occur. If the local

30 composition of the sealing glass is altered sufficiently during the sealing operation, a new phase may form which, because of thermal expansion mismatch may lead to fracture in the sealing area. Such a process would cause the sodium-sulfur cell to fail. We have provided glass stability thereby increasing its resistance to devitrification by the incorporation of a specific combination of modifying alkali earth oxides in a range from 15 weight percent to 40 weight

35 percent of the glass composition. The specific combination of these modifying oxides are calcium oxide, barium oxide and strontium oxide. The inclusion of this specific combination of modifying oxides insures that the glass

40 composition remains in the glass forming region despite slight changes in composition during the sealing operation. Additionally, the thermal expansion coefficient of our sealing glass closely matches that of both the beta-aluminas and the

45 alpha-alumina.

Our sodium resistant aluminoborate sealing glasses are also thermally compatible with various borosilicate glasses and a wide variety of metals, such as Kovar alloy, molybdenum, etc.,

50 developed for ceramic-to-metal seals. We have recently made successful ceramic-to-metal seals of alpha-alumina to Kovar alloy and alpha-alumina to molybdenum with our sodium resistant aluminoborate sealing glasses.

65 In the preparation of our sodium resistant

aluminoborate sealing glasses, we mix together the chemicals which on melting, decomposing and reacting yield 10—30 weight percent alumina, 35—50 weight percent boron oxide,

70 15—40 weight percent of a mixture of alkali earth oxides of calcium oxide, barium oxide and strontium oxide, 0—20 weight percent of silica, and 0—5 weight percent of a mixture of metal alkali oxides selected from the group consisting of

75 sodium oxide, lithium oxide, and potassium oxide. The mixed batch is then melted in an air atmosphere at a temperature in a range from 1000°C to 1300°C. The molten glass is poured into a mold to form the glass in a convenient

80 shape such as a block. The glass is then cooled to room temperature to provide the sodium resistant aluminoborate sealing glass of our invention.

When such sealing glass is used for sealing together two components, for example, the

85 flange and the outer wall of an ion-conductive tube in a sodium-sulfur battery, the glass is ground to reduce the above glass block to small particle size. A flange or ring of alpha-alumina is positioned around and adjacent the open end of the ion-conductive electrolyte tube of beta-

90 alumina. The flange has a lower inner portion which abuts against the outer wall of the tube while the inner, portion of the flange is recessed. The flange and tube are held in position by a

95 suitable fixture to form an assembly. The glass particles of the sealing glass are positioned in the recess between the outer surface of the tube and the upper portion of the adjacent flange. The tube and flange with the particles positioned

100 therebetween as above described, are then heated to a temperature of about 900°C in an air atmosphere to melt the glass particles into a molten state. The assembly is then cooled to room temperature with a resulting sodium

105 resistant aluminoborate sealing glass sealing the flange to the outer wall of the tube. A sodium-sulfur cell is then constructed in accordance, for example, with the above mentioned U.S. Patent No. 3,946,751.

110 Examples of our sodium resistant aluminoborate sealing glass made in accordance with our invention are set forth below:

Example I

A sodium resistant aluminoborate sealing glass

115 was formed by mixing together the chemicals which on melting, decomposing and reacting yield 19 weight percent alumina, 45 weight percent boron oxide, 6 weight percent calcium oxide, 12 weight percent barium oxide, 10 weight

120 percent strontium oxide and 8 weight percent silica. This mixed batch was heated to a temperature of 1100°C in an air atmosphere to provide molten glass. The molten glass was poured into a block-shaped mold and allowed to

125 cool. The resultant block was a sodium resistant aluminoborate sealing glass made in accordance with our invention.

Example II

A sodium resistant aluminoborate sealing glass

was formed by mixing together the chemicals which on melting, decomposing and reacting yield 19 weight percent alumina, 45 weight percent boron oxide, 7 weight percent calcium oxide, 6 weight percent barium oxide, 13 weight percent strontium oxide, and 10 weight percent silica. This mixed batch was heated to a temperature of 1100°C in an air atmosphere to provide molten glass. The molten glass was poured into a block shaped mold and allowed to cool. The resultant block was a sodium resistant aluminoborate sealing glass made in accordance with our invention.

Example III

A block of sodium resistant aluminoborate sealing glass made in accordance with Example I, was subjected for 160 hours at 350°C in sodium vapor. The sealing glass exhibited little, if any, discoloration. For comparison purposes, a high silica sealing glass was prepared in a conventional manner, which glass consisted of 50 weight percent silica, 10 weight percent alumina, 30 weight percent barium oxide and 10 weight percent boron oxide. This high silica glass was subjected in the same manner as our sealing glass to sodium vapors for 160 hours at 350°C. The high silica sealing glass turned dark brown indicating the presence of metallic sodium in the glass and thus providing a measure of sodium permeability.

Example IV

Blocks of sodium resistant aluminoborate sealing glass were prepared in accordance with Example I. These blocks were ground to a small particle size. Fifty sodium beta ion-conductive tubes were each provided with an alpha-alumina flange around its outer surface and adjacent its open end. Each flange had a lower portion which abutted the outer wall of the respective tube while the upper portion provided a recess between the outer wall of the tube and the flange. Sealing glass particles were positioned in each of these recesses. Each tube and its associated flange with sealing glass particles was held in

position by a fixture to provide an assembly. Each assembly was heated to a temperature of 900°C in an air atmosphere after which it was cooled to room temperature resulting in a sodium resistant aluminoborate sealing glass seal between the exterior wall of the tube and the inner surface of the flange.

Example V

Fifty sodium-sulfur cells employing the fifty sealed tubes and flanges from Example IV were made in accordance with the above mentioned U.S. Patent No. 3,946,751. These fifty cells were tested in actual operation for a period of six months. Subsequent investigation of these tubes showed no failures in the sodium resistant aluminoborate sealing glass seals. Further, such investigation showed that the sodium attack of the sealing glass was negligible during the cell testing.

Claims

1. A sodium resistant aluminoborate sealing glass comprising 10—30 weight percent alumina, 35—50 weight percent boron oxide, 15—40 weight percent of a mixture of alkali earth oxides of calcium oxide, barium oxide and strontium oxide, 0—20 weight percent of silica, and 0—5 weight percent of a mixture of alkali metal oxides of sodium oxide, lithium oxide, and potassium oxide.
2. A sodium resistant aluminoborate sealing glass as claimed in claim 1 consisting of 19 weight percent alumina, 45 weight percent boron oxide, 6 weight percent calcium oxide, 12 weight percent barium oxide, 10 weight percent strontium oxide, and 8 weight percent silica.
3. A sodium resistant aluminoborate sealing glass as claimed in claim 1 consisting of 19 weight percent alumina, 45 weight percent boron oxide, 7 weight percent calcium oxide, 6 weight percent barium oxide, 13 weight percent strontium oxide, and 10 weight percent silica.
4. A sodium resistant aluminoborate glass as claimed in claim 1 substantially as hereinbefore described in any one of the Examples.