Electrode unit for an electrochemical device

Description

The invention relates to an electrode unit for an electrochemical device, comprising (i) a solid electrolyte which divides a space for molten cathode material, selected from the group consisting of elemental sulfur and polysulfide of the alkali metal anode material, and a space for molten alkali metal anode material and (ii) a porous solid state electrode directly adjacent to the solid electrolyte within the space for the cathode material, with a non-electron-conducting intermediate layer S present between the solid state electrode and the solid electrolyte, wherein the intermediate layer S has a thickness in the range from 0.5 to 5mm and, before the first charge of the electrochemical device, has been impregnated fully with a polysulfide composition, comprising (A) pure polysulfides Met_2S_x with Met = alkali metal of the alkali metal anode material selected from lithium, sodium, potassium, and x is dependent on the alkali metal and is 2, 3, 4 or 5 for Na and is 2, 3, 4, 5, 6, 7, 8 for Li and is 2, 3, 4, 5, 6 for K, or (B) mixtures of the polysulfides of one and the same alkali metal from (A) with one another, to an electrochemical device comprising the electrode unit as defined in the claims, to a process for producing a non-electron-conducting intermediate layer S in an electrode unit as defined in the claims, which comprises subjecting the porous starting material that forms the non-electron-conducting intermediate layer S to a pressure of less than 1 atm and impregnating it with the molten polysulfide composition of the alkali metal that forms the alkali metal anode material comprising (A) pure polysulfides Met_2S_x with Met = alkali metal of the alkali metal anode material selected from lithium, sodium, potassium, and x is dependent on the alkali metal and is 2, 3, 4 or 5 for Na and is 2, 3, 4, 5, 6, 7, 8 for Li and is 2, 3, 4, 5, 6 for K, or (B) mixtures of the polysulfides of one and the same alkali metal from (A) with one another, to a process for first charging of an electrochemical device as defined in the claims, which comprises initially charging the space for the molten cathode material with a polysulfide compound (I) as a melt, comprising: (A) pure polysulfides Met_2S_x with Met = alkali metal of the desired alkali metal anode material, selected from lithium, sodium, potassium, x is dependent on the alkali metal and is 2, 3, 4 or 5 for Na and is 2, 3, 4, 5, 6, 7, 8 for Li and is 2, 3, 4, 5, 6 for K, or (B) mixtures of the polysulfides of one and the same alkali metal from (A) with one another and/or in each case with elemental sulfur or (C) mixtures of the particular alkali metal sulfide Met_2S with elemental sulfur and/or the polysulfides Met_2S_x mentioned in (A) or (B), and additionally installing, in the space for the molten anode material, an electron-conducting device in such a way that it touches the surface of the solid electrolyte facing the anode material at least in the lower region, connects cathode space and anode space to an electrical circuit and sends an electrical current through this electrochemical device, such that the polysulfide compound (I) is cleaved electrolytically, forming elemental sulfur in the cathode space and metallic alkali metal in the anode space, and to the use of a non-electron-conducting intermediate layer S in an electrode unit for an electrochemical device, comprising (i) a solid electrolyte which divides a space for molten cathode material - as defined herein - and a space for molten alkali metal anode material - as defined herein - and (ii) a porous solid state electrode which is separated from the solid electrolyte by a non-electron-conducting intermediate layer S, wherein the non-electron-conducting intermediate layer S has a thickness in the range from 0.5 to 5mm and, before the first charge of the

electron-conducting intermediate layer S, which is described in detail below, such that the following structure typically arises: solid electrolyte/intermediate layer S/porous solid state electrode, for example beta-alumina solid electrolyte/non-electron-conducting intermediate layer S/porous solid state electrode composed of graphite felt.

The porous solid state electrode, preferably the graphite or graphite felt, covers the surface of the solid electrolyte on the side facing the cathode material typically fully or else partly, for example to an extent of 50% to 100%, preferably to an extent of 90% to 100%, of the surface area, typically not including the base region of the solid electrolyte, for example the base of cylindrical tubes closed at one end, in the calculation.

The material – also called "starting material" herein – which, according to the invention, absorbs the ~~inventive~~ polysulfide compound to form the non-electron-conducting intermediate layer S is selected from alumina (Al_2O_3), silicon dioxide, for example glass fibers, mixed oxides of aluminum with silicon, silicates and aluminosilicates. These materials have virtually zero electrical conductivity under standard conditions, for example 25°C, 1 atm.

The starting material for the non-electron-conducting intermediate layer S and the non-electron-conducting intermediate layer S itself are typically porous having generally (i) an open porosity in the range from 50% to 99.99%, preferably 80% to 99%, more preferably 90% to 95%, the open porosity being calculated as follows: 1 – (bulk density of the specimen/density of the material that forms the specimen) x 100, and (ii) a mean pore diameter of typically in the range from 1 to 10 micrometers, measured by the method of optical microscopy.

Typically, the basis of the non-electron-conducting intermediate layer S is a flat structure – for example woven fabric, felt or mat – of fibers selected from the materials as described above, preferably selected from fibers of alumina, for example Saffil ® from Saffil, and/or silicon dioxide, for example glass fibers.

~~The~~According to the invention, the thickness of the non-electron-conducting intermediate layer S is ~~typically~~ in the range from 0.5 to 5 mm, preferably 1.0 to 3 mm, more preferably in the range from 1 to 2 mm.

The non-electron-conducting intermediate layer S is arranged between the porous solid state electrode and the solid electrolyte, and is virtually flush with the solid electrolyte surface.

The non-electron-conducting intermediate layer S typically covers virtually the entire area of the solid state electrode facing the solid electrolyte.

The non-electron-conducting intermediate layer S, before the first charge of the electrochemical device, has been completely impregnated with a polysulfide composition of the alkali metal that forms the alkali metal anode material, comprising (A) pure polysulfides Met_2S_x with Met = alkali metal of the alkali metal anode material selected from lithium, sodium, potassium, especially sodium, and x is dependent on the alkali metal and is 2, 3, 4 or 5, preferably 3, 4 or 5, especially

for first charging of an electrochemical device is conducted as described above, with the following differences:

The solid electrolyte is a cylindrical tube closed at one end, as described above, composed of beta-alumina.

The anode space is the interior of the cylindrical tube closed at one end, in which the molten alkali metal anode material sodium is produced in the course of cell charging.

The electron-conducting device is arranged coaxially within the cylindrical tube closed at one end, in the form of a solid or hollow cylindrical body having dimensions that are similar but smaller than those of the cylindrical tube closed at one end ("displacer", reference numeral 1 in figure 1) such that an annular gap forms between the inner wall of the solid electrolyte and the outer wall of the displacer, and the displacer touches the inner surface of the solid electrolyte, at least in the lower region, at at least one point, for example via spring elements, such that an electrical contact forms. The displacer is typically manufactured from a metal, for example aluminum, steel, stainless steel or other metals resistant to the alkali metals mentioned.

The cathode space in variant 1 begins at the outer surface of the cylindrical tube closed at one end and is bounded on the outside by a housing, for example of steel, stainless steel, chrome-plated aluminum or other, preferably corrosion-resistant, materials, as shown, for example, in figure 1 (reference numeral 8).

Applied to the outer surface of the cylindrical tube of the solid electrolyte which is closed at one end are, as described above, firstly the non-electron-conducting intermediate layer S and, on top of that, the porous solid state electrode, shown, for example, in figure 1 by reference numeral 2 (porous solid state electrode) and reference numeral 7 (non-electron-conducting intermediate layer S).

The molten cathode material is selected from (A) pure polysulfides Na_2S_x with x = 2, 3, 4, or 5, preferably 3, 4 or 5, especially 4, or (B) mixtures of the polysulfides from (A) with one another and/or in each case with elemental sulfur or (C) mixtures of Na_2S with elemental sulfur and/or the polysulfides Na_2S_x mentioned in (A) or (B). Preferred molten cathode material is the aforementioned components (A) or (B).

Both molten cathode material and molten anode material are connected to a circuit in an electrically conductive manner.

The present application also provides for the use of a non-electron-conducting intermediate layer S in an electrode unit for an electrochemical device, comprising (i) a solid electrolyte which divides a space for molten cathode material and a space for molten alkali metal anode material, and (ii) a porous solid state electrode which is separated from the solid electrolyte by a non-electron-conducting intermediate layer S, wherein the intermediate layer S has a thickness in the range from 0.5 to 5mm and, before the first

Claims

1. An electrode unit for an electrochemical device, comprising (i) a solid electrolyte which divides a space for molten cathode material, selected from the group consisting of elemental sulfur and polysulfide of the alkali metal anode material, and a space for molten alkali metal anode material and (ii) a porous solid state electrode directly adjacent to the solid electrolyte within the space for the cathode material, with a non-electron-conducting intermediate layer S present between the solid state electrode and the solid electrolyte, wherein this intermediate layer S has a thickness in the range from 0.5 to 5mm and, before the first charge of the electrochemical device, has been impregnated fully with a polysulfide composition, comprising (A) pure polysulfides Met_2S_x with Met = alkali metal of the alkali metal anode material selected from lithium, sodium, potassium, and x is dependent on the alkali metal and is 2, 3, 4 or 5 for Na and is 2, 3, 4, 5, 6, 7, 8 for Li and is 2, 3, 4, 5, 6 for K, or (B) mixtures of the polysulfides of one and the same alkali metal from (A) with one another.

~~2. The electrode unit according to claim 1, wherein the intermediate layer S has a thickness in the range from 0.5 to 5 mm.~~

3.2. The electrode unit according to claim 1 ~~or 2~~, wherein the basis of the non-electron-conducting intermediate layer S is a flat structure of fibers selected from alumina (Al_2O_3), silicon dioxide, mixed oxides of aluminum with silicon, silicates and aluminosilicates.

4.3. The electrode unit according to claims 1 orto ~~3~~2, wherein the solid electrolyte is a cylindrical shaped body closed at one end.

5.4. An electrochemical device comprising the electrode unit as defined in claims 1 to 43.

6.5. The electrochemical device according to claim ~~5~~4, wherein the electrochemical device is a sodium-sulfur cell.

~~7~~.6. A process for producing a non-electron-conducting intermediate layer S in an electrode unit as defined in claims 1 to 43, which comprises subjecting the porous starting material that forms the non-electron-conducting intermediate layer S to a pressure of less than 1 atm and impregnating it with the molten polysulfide composition of the alkali metal that forms the alkali metal anode material comprising (A) pure polysulfides Met_2S_x with Met = alkali metal of the alkali metal anode material selected from lithium, sodium, potassium, and x is dependent on the alkali metal and is 2, 3, 4 or 5 for Na and is 2, 3, 4, 5, 6, 7, 8 for Li and is 2, 3, 4, 5, 6 for K, or (B) mixtures of the polysulfides of one and the same alkali metal from (A) with one another.

~~8~~.7. A process for first charging of an electrochemical device as defined in claims ~~5~~4 and ~~6~~5, which comprises initially charging the space for the molten cathode material with a

polysulfide compound (I) as a melt, comprising: (A) pure polysulfides Met_2S_x with Met = alkali metal of the desired alkali metal anode material, selected from lithium, sodium, potassium, x is dependent on the alkali metal and is 2, 3, 4 or 5 for Na and is 2, 3, 4, 5, 6, 7, 8 for Li and is 2, 3, 4, 5, 6 for K, or (B) mixtures of the polysulfides of one and the same alkali metal from (A) with one another and/or in each case with elemental sulfur or (C) mixtures of the particular alkali metal sulfide Met_2S with elemental sulfur and/or the polysulfides Met_2S_x mentioned in (A) or (B), and additionally installing, in the space for the molten anode material, an electron-conducting device in such a way that it touches the surface of the solid electrolyte facing the anode material at least in the lower region, connects cathode space and anode space to an electrical circuit and sends an electrical current through this electrochemical device, such that the polysulfide compound (I) is cleaved electrolytically, forming elemental sulfur in the cathode space and metallic alkali metal in the anode space.

~~9.~~8. The use of a non-electron-conducting intermediate layer S in an electrode unit for an electrochemical device, comprising (i) a solid electrolyte which divides a space for molten cathode material - as defined in claim 1 - and a space for molten alkali metal anode material, and (ii) a porous solid state electrode which is separated from the solid electrolyte by a non-electron-conducting intermediate layer S, wherein the non-electron-conducting intermediate layer S, before the first charge of the electrochemical device, has been impregnated fully with a polysulfide composition of the alkali metal that forms the alkali metal anode material, comprising (A) pure polysulfides Met_2S_x with Met = alkali metal of the alkali metal anode material selected from lithium, sodium, potassium, x is dependent on the alkali metal and is 2, 3, 4 or 5 for Na and is 2, 3, 4, 5, 6, 7, 8 for Li and is 2, 3, 4, 5, 6 for K, or (B) mixtures of the polysulfides of one and the same alkali metal from (A) with one another.