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(71) Applicants
Anselm Thomas Kuhn,
105 Whitney Drive, Old
Stevenage, Hertfordshire,
Alfred Chan Chung
Tseung, 60 Grove Avenue,
London, N10 2AN,
Christopher Francis
Brammall, 39 Wood Field
Gardens, New Malden,
Surrey
(72) Inventors
Anselm Thomas Kuhn,
Alfred Chan Chung
Tseung,
Christopher Francis
Brammall
(74) Agent
P. W. Neville

(54) Metal Silicate Catalytically Active Anode

(57) An example comprises a nickel mesh substrate having coated thereon a dispersion of 1 part of polytetrafluoroethylene binder plus 10 parts of cobalt silicate at a rate of 21 mg cobalt silicate/cm^2 of mesh. The silicate is reduced in hydrogen sufficiently to improve its electric conductivity.

SPECIFICATION

Catalytically Active Anode

This invention relates to a catalytically active anode. Many suggestions have been made for improving anodes, especially in brine electrolysis. Thus, as one example among many, US Patent Specification 4040934 discloses an anode having a conductive substrate on the surface of which there is coated a "metal silicide", the metal being one of Pt, Pd, Ir, Rh, Cr, Co, Ni, Ru, Ti, V, Zr, Nb, Hf, Ta and W.

The activity of these anodes has now been discovered to stem from the formation of certain compounds thereon in use, and the invention consists in the making and exploitation of this discovery to make better anodes. Thus, certain "metal silicide" anodes have been discovered to develop, in use, superficial metal silicates which are electrocatalytically active.

Accordingly the invention consists in a catalytically active anode comprising at its surface an at least semiconductive water-insoluble metal silicate. Preferably, the anode is made by dispersing the metal silicate in a non-conductive binder, and applying the dispersion to a conductive substrate. Preferably, the silicate is reduced sufficiently to improve its electrical conductivity. Preferably the binder is hydrophobic, for example polytetrafluoroethylene, but the dispersion as a whole should not be excessively hydrophobic.

The metal silicate may have a spinel or olivine structure, both of which are reported to have been synthesised. The olivine is convenient. It is preferably cobalt orthosilicate (Co_2SiO_4) or may be nickel silicate (Ni_2SiO_4). Other silicates which could be used are those of other transition metals such as iron, or of copper or precious metals. Mixed silicates may also be used.

The substrate is preferably in the form of an electrically conductive sheet (foraminate or otherwise), slit metal or mesh, preferably of nickel. If of iron, the substrate preferably contains under 1.5% (more preferably under 0.3%) of carbon. Preferably the weight ratio of binder to metal silicate is from 1:3, more preferably from 1:5, to 1:20 and the dispersion is preferably applied to give a coating of from 5 mg to 50 mg of the metal silicate per square centimetre of the substrate.

The invention extends to a catalytically active anode made as set forth above, and to an electrolytic cell including a cathode and such an anode. The invention further extends to a method of electrolysis using this cell, especially of aqueous solution, e.g. aqueous alkali.

The invention will now be described by way of example.

Making an Anode

Although known syntheses of transition metal silicates include precipitation from sodium silicate solution, and gelling using tetraethyl orthosilicate, it was found that solid state sintering gave the best results.

Cobalt nitrate was ground with a stoichiometric amount of silica with a pestle and mortar. The mixture of cobalt nitrate and silica was transferred to an evaporating basin, gently heated to allow the nitrate to dissolve in its own water of crystallisation and then vigorously heated by bunsen burner to dry and decompose the nitrate to its oxide. The resultant powder was ground again and then heated at 1000°C for 24 hours, to promote the reaction

$$2CoO+SiO_2 \rightarrow Co_2SiO_4.$$

The product was ground again, washed with 5M KOH and then with concentrated HNO_3 to remove any unreacted silica or cobalt oxide, then washed with water, dried, ground again and put in a dry sample bottle. That the product was cobalt silicate (olivine structure) was confirmed by X-ray powder diffraction.

It was found that the cobalt silicate prepared had a specific conductivity of $2\times10^{-6}\Omega^{-1}cm^{-1}$ or lower, which was far too low to contemplate its use as an electrocatalyst. Therefore it was decided to try to improve the conductivity by standard methods used in semiconductor electrochemistry. It was found that heating under argon did not improve the conductivity, but the conductivity of cobalt silicate heated at 800°C for 2 hours under hydrogen rose to $6\times10^{-2}\Omega^{-1}cm^{-1}$. X-ray photos (and subsequent electrochemical performance) showed that the silicate had not been reduced by any degree to the metal, or to metal oxide and silica. (Parallel experiments on iron silicate when treated in the same way showed some iron present, and nickel silicate was completely reduced to metal and silica. However the literature on the reduction of silicates by CO indicates that if the conditions are altered then conducting non-reduced iron and nickel silicates may be obtained).

A mixture of the treated cobalt silicate, polytetrafluoroethylene and water was dispersed in an ultrasonic bath, and the dispersion painted onto a nickel wire mesh 1 cm square. The electrode so formed was dried and cured for 1 hour at 300°C. Initially a cobalt silicate: polytetrafluoroethylene ratio of 10:3 was used, but as this proved to be too hydrophobic, the present electrode used a ratio of 10:1, giving a cobalt silicate loading of 21 mg/cm².

Electrolysis

An aqueous solution of 5M KOH was electrolysed at 40°C in a cell having a nickel mesh cathode and the above anode. (The anode had previously been anodised for 2 hours at 2V vs the dynamic hydrogen electrode, to activate it, possibly by forming higher oxides on its surface and hydrophilising it). The current was held at 1 amp. Oxygen was evolved at the anode, at which the voltage vs. the dynamic hydrogen electrode rose from an initial 1700 mV, neglecting early fluctuations, to 1740 mV after 40 days, possibly due to formation of a poorly conductive nickel oxide at the interface between screen and cobalt silicate.

An identical cell (but with cobalt silicate loading of 14 mg/cm^2) was run at 25°C, 50°C and 70°C at up to $2\frac{1}{2}$ A/cm^2. At 2 A/cm^2, the iR-corrected voltages at the anode vs. the dynamic hydrogen electrode were 1710 mV, 1650 mV and 1620 mV respectively.

(Parallel experiments on iron silicate suggested that the iron silicate might be corroding at up to 6 mg/cm^2/week at 1 A/cm^2, before and after which the voltage was 1680 mV and 1720 mV respectively).

Claims

1. A catalytically active anode comprising, at its surface, an at least semiconductive water-insoluble metal silicate.

2. An anode according to Claim 1, wherein the metal is cobalt.

3. An anode according to Claim 1, wherein the metal is nickel.

4. An anode according to Claim 1, wherein the metal is a transition metal or a precious metal.

5. An anode according to Claim 1, wherein the metal is copper.

6. An anode according to Claim 4, wherein the metal is iron.

7. An anode according to any preceding claim, wherein the anode comprises mixed silicates.

8. An anode according to any preceding claim, wherein the metal silicate has a spinel or olivine structure.

9. An anode according to any preceding claim, wherein the metal silicate is dispersed in a non-conductive binder, and the dispersion is applied to a conductive substrate.

10. An anode according to Claim 9, wherein the binder is hydrophobic.

11. An anode according to Claim 10, wherein the binder is polytetrafluoroethylene.

12. An anode according to Claim 9, 10 or 11, wherein the weight ratio of binder to metal silicate is from 1:3 to 1:20.

13. An anode according to Claim 12, wherein the said weight ratio is from 1:5 to 1:20.

14. An anode according to any of Claims 9 to 13, wherein the substrate is in the form of an electrically conductive sheet, slit metal or mesh.

15. An anode according to Claim 14, wherein the substrate is of nickel.

16. An anode according to any of Claims 9 to 15, wherein the dispersion is applied such as to give a coating of from 5 mg to 50 mg of the metal silicate per square centimetre of the substrate.

17. An anode according to Claim 9, substantially as hereinbefore described with reference to the example designated "Making an Anode".

18. Making an anode as defined in any of Claims 9 to 17, comprising dispersing the metal silicate in a non-conductive binder and applying the dispersion to a conductive substrate.

19. Making an anode according to Claim 18, further comprising reducing the silicate sufficiently to improve its electrical conductivity.

20. Making an anode according to Claim 18 or 19, substantially as hereinbefore described with reference to the example designated 'Making an Anode'.

21. An anode made according to Claim 18, 19 or 20.

22. An electrolytic cell comprising a cathode and an anode according to any of Claims 1 to 17 or 21.

23. A method of electrolysis, when performed in the cell according to Claim 22.

24. A method according to Claim 23, wherein the electrolyte comprises an aqueous solution.

25. A method according to Claim 24, wherein the aqueous solution is aqueous alkali.

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