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(54) Electrosynthesis of borohydride

(57) A method for producing borohydride by causing current to flow in an electrolytic cell between an anode and a cathode, wherein a solution of a boron-containing compound is in contact with the cathode, and wherein the cathode comprises a conductive material having activity as a high hydrogen overpotential electrode.

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Description

[0001] The present invention is directed to a method for one-step electrosynthesis of borohydride.

[0002] Several electrolytic processes for production of borohydride have been described in the literature, for example, in U.S. Pat. No. 3,734,842, to Cooper. However, a study performed by E.L. Gyenge and C.W. Oloman, and documented in *Journal of Applied Electrochemistry,* vol. 28, pp. 1147-51 (1998), demonstrated that the method of Cooper, as well as several other published electrosyntheses of borohydride, actually does not produce measurable amounts of borohydride.

[0003] The problem addressed by this invention is the need for an electrochemical synthesis of borohydride.

STATEMENT OF THE INVENTION

[0004] The present invention is directed to a method for producing borohydride. The method comprises causing current to flow in an electrolytic cell between an anode and a cathode, wherein a solution of a boron-containing compound is in contact with the cathode, and wherein the cathode comprises a conductive material having activity as a high hydrogen overpotential electrode.

DETAILED DESCRIPTION OF THE INVENTION

[0005] As used in this application, "borohydride" means the tetrahydridoborate ion, BH_4^-.

[0006] In the electrolytic reaction of the present invention, borohydride anions formed at the cathode are prevented from migrating to the anode. In one embodiment of the invention, this is accomplished by providing a cation-selective ion exchange membrane to separate the anode and cathode compartments. The cation-selective membrane allows sodium, or other cations, to cross into the cathode compartment to balance the charge that would otherwise accumulate from production of hydroxide and borohydride at the cathode. In another embodiment, the anolyte is acidic, and protons cross the membrane into the cathode compartment and maintain a relatively neutral pH therein. As an alternative to an ion-exchange membrane, a microporous separator may be used to allow ions to cross in either direction; in this case, borohydride would cross over into the anode compartment to some extent and be oxidized.

[0007] In one embodiment of the invention, the electrolytic reaction occurs in a non-aqueous solvent in which borohydride is soluble, e.g., C_1-C_4 aliphatic alcohols, e.g., methanol, ethanol; ammonia; C_1-C_4 aliphatic amines; glycols; glycol ethers; and polar aprotic solvents, for example, dimethylformamide (DMF), dimethylacetamide (DMAc), dimethyl sulfoxide, hexamethyl phosphoramide (HMPA), and combinations thereof. Preferably, the non-aqueous solvent is methanol, ethanol, DMF, HMPA, or combinations thereof. Preferably, the amount of water present in non-aqueous solvents is less than 1%, more preferably less than 0.1%, more preferably less than 100 ppm, and most preferably the non-aqueous solvents are substantially free of water.

[0008] In another embodiment, the electrolytic reaction occurs in an aqueous solvent or an aqueous/organic solvent mixture having more than 1% water. Organic solvents used in an aqueous/organic solvent mixture are those having sufficient solubility in water to form a solution.

[0009] Preferably, when protic solvents are used, especially water, methanol or ethanol, alkali is present to stabilize the borohydride, preferably at least 0.1 N alkali.

[0010] Preferably, the boron-containing compound of the present invention is a salt or acid of a boron-containing ion, or a trialkyl borate, $B(OR)_3$, wherein R preferably is methyl or ethyl. Preferably, the boron-containing ions used in the present invention are complex ions containing only boron and oxygen. More preferably, the boron-containing ions are borate, tetraborate, or metaborate. Most preferably, the boron-containing ion is metaborate or tetraborate.

[0011] A synthetic polymer used in the present invention includes, for example, polyolefins, e.g., polymers made from monomers comprising ethylene, propylene, other ethylenically unsaturated hydrocarbons or mixtures thereof; polymers made from monomers comprising halogenated olefins, e.g., halogenated ethylenes; polystyrenes; polyethers; polyvinyl alcohols; polyamides; and mixtures thereof. In one embodiment of the invention, an addition polymer made from ethylenically unsaturated monomers is used. In one embodiment of the invention, a hydrophobic synthetic polymer is used, e.g., an addition polymer substantially free of atoms other than carbon, hydrogen and halogen atoms. In one preferred embodiment, a hydrophobic synthetic polymer used in the present invention is an addition polymer comprising at least 50% by weight of monomer units derived from one or more fluorinated ethylene monomers, e.g., tetrafluoroethylene, 1,1-diffuoroethylene, or trifluoroethylene. More preferably, the hydrophobic synthetic polymer comprises at least 75% of monomer units derived from one or more fluorinated ethylene monomers. Most preferably, the hydrophobic synthetic polymer is poly(tetrafluoroethylene) (PTFE).

[0012] For the purposes of this invention, a high hydrogen overpotential electrode is one where the reduction potential for electrolysis of water to form hydrogen under the reaction conditions is approximately equal to, or more negative than the reduction potential for borate reduction. The theoretical reduction potential for borate reduction is -1.24 volts vs. a standard hydrogen electrode ("SHE"). In one embodiment of the invention, the high hydrogen overpotential electrode comprises a metal inherently having such activity, for example, lead, zinc, cadmium, mercury and indium. In another embodiment, the electrode comprises a high-surface-area electrode, preferably a carbon high-surface-area electrode. Examples of suitable carbons are carbon cloths and felts, vitreous carbon, and reticulated vitreous carbon. The term "high-surface-area" means having a surface area of at least 0.005 m^2/g. Reticulated vitreous carbon foam having approximately 10 pores per inch typically has a surface area of about 0.01 m^2/g. Carbon felt or cloth typically has a surface area of about 0.5 m^2/g. Carbon black and gas diffusion electrodes fabricated with carbon black typically have a surface area of about 200 m^2/g or more.

[0013] A "nickel screen electrode" is an expanded nickel mesh. An example is the Delker™ 416 nickel mesh, having diamond-shaped openings, 0.416 inches x 0.170 inches, with a strand thickness of 0.005 inches, and approximately 75% open space.

[0014] Preferably a cathode that comprises a synthetic polymer and a conductive material having activity as a high hydrogen overpotential electrode comprises a mixture of the synthetic polymer and the conductive material supported on a metal or graphite base electrode. Preferably the conductive material is a metal. Preferably, the cathode is formed by plating from a mixture of polymer particles suspended in water and a solution containing a salt of the metal. The base electrode onto which the mixture is plated preferably comprises the same metal as the metal salt which is plated.

[0015] When the cathode comprises a synthetic polymer and a conductive material having activity as a high hydrogen overpotential electrode, preferably the current density is no greater than 100 mA/cm^2, more preferably no greater than 75 mA/cm^2, and most preferably no greater than 50 mA/cm^2.

[0016] In one embodiment of the invention, the cathode comprises a synthetic polymer and at least one metal on the surface of a high surface-area electrode. In this embodiment, the metal has activity as a high hydrogen overpotential electrode due to the presence of the synthetic polymer. The metal preferably is nickel, an alloy comprising two metals, or a metal inherently having activity as a high hydrogen overpotential electrode. An alloy comprising two metals, A and B, preferably is of the form AB_5, AB, A_2B or AB_2. Preferably at least one of the metals is a transition metal. In one embodiment, at least one of the metals is a rare earth metal. In one embodiment, A and B are both transition metals. Preferably, one of the metals is La, Ni, Ti or Zr. In one embodiment, AB_5 is $LaNi_5$, optionally with additional metals, e.g., Sn, Ge, Al or Cu. In one embodiment in which the alloy is of form AB_2, the metals are Ti and Zr, optionally with additional metals, e.g., Mn, Cr, Fe, V or Ni. In one embodiment in which the alloy is of form A_2B, the alloy is Mg_2Ni. In one embodiment in which the alloy is of form AB, it is FeTi.

[0017] A gas diffusion electrode (GDE) is one that enables direct electronic transfer from a gas phase to or from a solid phase. The GDE also provides a path for ionic transfer. A GDE typically comprises a conductive porous support, e.g., carbon cloth, carbon paper or metal mesh. The GDE often has a wet-proofing layer of carbon black, and optionally additional layers of wet-proofing. Finally, an electrocatalyst layer typically is applied to the surface, or is applied to carbon black prior to electrode assembly. The electrocatalyst facilitates reduction of boron compounds over reduction of water. The wet-proofing material may be a synthetic polymer, as described above, e.g., PTFE, which may be applied as an emulsion in water. A heat treatment often is applied as a final step to soften the polymer and embed the materials into a single substrate. Optionally the GDE comprises a highly dispersed metal electrocatalyst which can act as a very high surface area cathode. Hydrogen generated at the cathode, or alternatively, fed to the back of the electrode, may provide an activated catalyst which allows in situ hydride formation.

[0018] In an embodiment of the invention in which a gas diffusion electrode comprising a metal electrocatalyst is used, preferably the current density is greater than 120 mA/cm^2. Preferably the amount of metal which is present on the surface of the GDE is less than 2 mg/cm^2.

[0019] In aqueous systems, the predominant anode reaction is the electrolysis of water to form oxygen and protons. If the anolyte is acidic, protons will transport across the separator and neutralize the hydroxide that is generated at the cathode along with borohydride. If the anolyte is basic, the protons will neutralize the hydroxide in the anode compartment and sodium will transport across the separator to make byproduct sodium hydroxide. In one embodiment, the anode is a non-corroding material, for example, platinized titanium or iridium oxide on titanium. If the anolyte is basic, a lower-cost material would be quite stable, e.g., nickel. In a non-aqueous system, the anode could be a corrosion-resistant metal, e.g., platinum.

[0020] In one embodiment, the anolyte is an aqueous sodium salt, e.g., sodium hydroxide, sodium carbonate or sodium bicarbonate. Protons generated would then form stable species like water or carbon dioxide. Alternatively, any aqueous mineral acid would be suitable. In the case of a non-aqueous solvent, an organic-soluble conductive sodium salt would be suitable, e.g., a sodium alkoxide, or a lithium salt soluble in the non-aqueous solvent.

[0021] Other components may be used in the method of this invention to improve yield of borohydride, including additives that would improve solvation in non-aqueous systems; lithium or ammonium salts to raise hydrogen overpotential; and redox species, e.g., naphthalene or anthracene.

EXAMPLES

Example 1

[0022] Analytical Method for Borohydride Determination: The method of M.V. Mirkin and A.J. Bard, *Analytical Chem.,* vol. 63, pp. 532-33 (1991) was modified such that borohydride was oxidized at a gold rotating disk electrode (800 rpm) at approximately -0.150 V vs. a saturated calomel electrode (SCE). The height of the wave is dependent on the square root of the rotation rate and independent of the scan rate. The voltammetric sweep was performed at 100 mV/sec. The sensitivity of this method allows borohydride to be detected at levels below 1 ppm.

[0023] Experiments were performed in small divided glass H-cells when utilizing non-porous cathodes, and in the ASTRIS QUICKCELL 200 test cell, which has two acrylic compartments which individually feed to opposite sides of a membrane separator, when utilizing gas diffusion electrodes. Catholyte volumes were from 75 to 125 mL, and anolyte volumes from 35-55 mL. Some of the experiments were performed using PTFE-nickel composite electrodes. Preparation of these electrodes is similar to that described in Y. Kunugi et al., *J. Electroanal. Chem.,* vol. 313, pp. 215-25 (1991). To a nickel sulfamate bath (225 g $Ni(NH_2SO_3)_2$ and 20 g H_3BO_3 in 0.5 L H_2O) was added 80 mL of PTFE solution (TEFLON 30b solution - 30% TEFLON powder in H_2O). The composite cathode was prepared by plating the PTFE-nickel material from the bath onto a nickel plate (5 cm^2) at 20 mA/cm^2 for 1400 coulombs of charge. Borate reduction was then performed in a glass H-cell (1.0 M tetramethylammonium hydroxide (TMAH), 0.5 M H_3BO_3 catholyte, NAFION 324 cation exchange membrane (available from DuPont Co.), 1.0 M NaOH anolyte, room temperature, platinum anode).

[0024] The electrode made with Misch metal ($LaNi_5$) was prepared by grinding Misch metal and sieving to 100 mesh, thus providing a maximum particle size of 150 micron. An electrode was prepared by adding polyvinyl alcohol powder to 5% by weight and compressing onto a nickel screen and heat treating to provide a homogeneous electrode. The Misch metal concentration of the electrode was 425 mg/cm^2.

[0025] All experiments are described in Table 1. All experiments utilized a NAFION 324 cation exchange membrane, with a 1.0 M NaOH anolyte and a Pt or Pt/Nb anode, under current control with a DC power supply. The initial experiment, utilizing TMAH, showed the presence of borohydride with the cyclic voltammetric analysis method. The peak for borohydride was shifted from -0.15 V to -0.10 V, which is believed to be due to the higher concentration of hydroxide present in the actual sample from the electrolysis.

Table 1

Cathode	Catholyte	Current Density (mA/cm^2)	Charge, Coul.	BH_4^- Current Eff. (%)
PTFE-Ni	1.0M TMAH, 0.5M H_3BO_3	50	3154	2.9
PTFE-Ni	1.0M TMAH, 0.5M H_3BO_3	120	3780	<0.05
PTFE-Ni	1.0M NaOH, 0.5M H_3BO_3	50	2225	<0.05
PTFE-Ni	1.0M NaOH, 0.5M H_3BO_3	150	2900	<0.05
Ni/C GDE, 1.0 mg Ni/cm^2	1.0M NaOH, 0.5M H_3BO_3	80	3200	<0.05
Au/C GDE, 0.22 mg Au/cm^2	1.0M NaOH, 0.5M H_3BO_3	40	2501	<0.05
Au/C GDE, 0.22 mg Au/cm^2	1.0M NaOH, 0.5M H_3BO_3	160	2713	<0.05
Raney Ni GDE, 300 mg Ni/cm^2	1.0M NaOH, 0.5M H_3BO_3	25	2100	<0.05
Raney Ni GDE, 300 mg Ni/cm^2	1.0M NaOH, 0.5M H_3BO_3	100	2400	<0.05
Rh/C GDE, 5 mg Rh/cm^2	1.0M NaOH, 0.5M H_3BO_3	25	2250	<0.05

Table 1 (continued)

Cathode	Catholyte	Current Density (mA/cm^2)	Charge, Coul.	BH_4^- Current Eff. (%)
Zn/Ni screen, 300 mg/cm^2	1.0M NaOH, 0.5M H_3BO_3	40	2484	<0.05
Zn/Ni screen, 300 mg/cm^2	1.0M NaOH, 0.5M H_3BO_3	90	2429	<0.05
NiO-Co_2O_3/C GDE, 3 mg/cm^2	1.0M NaOH, 0.5M H_3BO_3	30	2497	<0.05
NiO-Co_2O_3/C GDE, 3 mg/cm^2	1.0M NaOH, 0.5M H_3BO_3	90	2429	<0.05
Ni/C Felt	10.0M NaOH, 0.5M H_3BO_3, 1% TMAH	30	2536	<0.05
$LaNi_5$/Ni Screen	10.0M NaOH, 0.5M H_3BO_3, 1% TMAH	50	2498	0.10
PTFE-Ni	10.0M NaOH, 0.5M H_3BO_3, 1% TMAH	30	2250	<0.05
Ni/C GDE, 1.0 mg Ni/cm^2	10.0M NaOH, 0.5M H_3BO_3, 1% TMAH	150	3421	0.15
Ni/C GDE, 2.0 mg Ni/cm^2	10.0M NaOH, 0.5M H_3BO_3, 1% TMAH	30	2625	<0.05
Ni/C GDE, 2.0 mg Ni/cm^2	10.0M NaOH, 0.5M H_3BO_3, 1% TMAH	120	3416	<0.05

Example 2

[0026] Electrode Preparation for Platinum/Palladium Alloy Plated Graphite Felt: Graphite felt was washed with dilute hydrochloric acid and then water to remove any metal ion impurities present. The felt was then plated with a platinum/palladium alloy. The plating was performed using a plating bath of the following composition:

$(NH_4)_2Pd(NO_2)_2$	5 g/L
$(NH_4)_2Pt(NO_2)_2$	0.3 g/L
$KHPO_4$	5 g/L

The bath was adjusted to pH 9 using ammonium hydroxide.

[0027] Plating was performed at 90°C using a constant current of 20 mA/cm^2 and a charge of 2000 coulombs passed. The plating was gray in appearance and concentrated at the outer surface of the felt.

[0028] All other electrodes used in this study were not pretreated except for acid washing to clean the surface.

[0029] General Electrolysis Procedure: A typical electrolysis was performed in a two-compartment glass cell divided with a NAFION 417 membrane (available from DuPont Co.). The anolyte consisted of 1 M sodium hydroxide (80 mL) and the anode material was platinized titanium or nickel. Unless specified otherwise, the catholyte was 25% by weight sodium metaborate adjusted to pH 11-12 with sodium hydroxide. The electrolysis was carried out at constant current.

[0030] Analytical Procedure: The amount of borohydride in the catholyte was determined indirectly by allowing it to react with cyclohexanone and determining the amount of cyclohexanol formed by gas chromatography. A 5 mL sample of the catholyte was reacted with 5 mL of a solution containing 2% by weight cyclohexanone in methanol. After reaction with the large excess of cyclohexanone, the mixture was injected directly into a gas chromatograph. The cyclohexanol peak was compared to the cyclohexanol peaks determined by reacting aqueous borate solution containing known amounts of borohydride.

[0031] The results of several experiments are presented in Table 2.

Table 2

Cathode	Catholyte	Current Density (mA/cm^2)	BH_4^- Current Eff. (%)
Gr felt plated with Pt/Pd	25% $NaBO_2$/pH 11-12	5	0.42
Pt flag	25% $NaBO_2$/pH 11-12	5	0.65
Gr felt	25% $NaBO_2$/pH 11-12	5	0.42
Gr felt	25% $NaBO_2$/pH 11-12	1	1.3
Pb flag	25% $NaBO_2$/pH 11-12	5	0.7
Zn flag	25% $NaBO_2$/pH 11-12	5	0.44
Ni flag	25% $NaBO_2$/pH 11-12/5% TMAH	5	0.5
Gr=graphite			

Claims

1. A method for producing borohydride; said method comprising causing current to flow in an electrolytic cell between an anode and a cathode, wherein a solution of a boron-containing compound is in contact with the cathode, and wherein the cathode comprises a conductive material having activity as a high hydrogen overpotential electrode.

2. The method of claim 1 in which the cathode further comprises a synthetic polymer.

3. The method of claim 2 in which the synthetic polymer is PTFE.

4. The method of claim 1 in which the cathode comprises lead, zinc, cadmium, mercury or indium.

5. The method of claim 1 in which the cathode comprises carbon having activity as a high hydrogen overpotential electrode.

6. The method of claim 5 in which the cathode comprises high-surface-area carbon.

7. A method for producing borohydride; said method comprising causing current to flow in an electrolytic cell between an anode and a cathode, wherein a solution of a boron-containing compound is in contact with the cathode, and wherein the cathode comprises a synthetic polymer and at least one metal on the surface of a high surface-area electrode.

8. The method of claim 7 in which said at least one metal comprises nickel.

9. The method of claim 7 in which the high surface-area electrode is a nickel screen electrode or a carbon gas diffusion electrode.

10. The method of claim 7 in which said at least one metal comprises an alloy of two transition metals.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 05 25 2121

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	PATENT ABSTRACTS OF JAPAN vol. 2003, no. 12, 5 December 2003 (2003-12-05) & JP 2003 247088 A (NISSAN MOTOR CO LTD), 5 September 2003 (2003-09-05) * abstract * -----	1,4,5	C25B1/00 C25B1/14
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TECHNICAL FIELDS SEARCHED (Int.Cl.7)

C25B

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	16 June 2005	Groseiller, P

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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& : member of the same patent family, corresponding document

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 05 25 2121

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