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Attempts to cathodically reduce boron oxides to borohydride in aqueous solution

J. McLafferty, S. Colominas, D.D. Macdonald*

Center for Electrochemical Science and Technology, Department of Materials Science and Engineering, Pennsylvania State University, University Park, PA 16802, United States

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ABSTRACT

Sodium borohydride is being considered as a chemical hydrogen storage material (hydrogen being released through hydrolysis) and as an anodic fuel for fuel cells. However, the current cost of sodium borohydride is prohibitively high for automotive applications. Thus, there is interest in recycling the by-product of the hydrolysis or oxidation reaction, sodium metaborate. Numerous patents claim that this reaction is feasible in aqueous solution. Here, we report extensive experiments based upon methods outlined in the patents (particularly, the so-called direct reduction using high overpotential cathode materials). We also attempt to address concerns not discussed in the patents. In particular, to the authors' knowledge, previous reports have not addressed electrostatic repulsion of metaborate anion from the cathode. We further report several methods that were designed to overcome this problem: (1) use of a cathode material having a very negative potential of zero charge, (2) modification of the electrical double layer by using specifically adsorbing tetraalkylammonium hydroxides, (3) use of a rectangular wave pulse, and (4) use of chemically modified cathodes. None of these methods produced measurable quantities of borohydride. We then speculate as to why this reaction is not feasible, at least in aqueous solutions.

1. Introduction

Sodium borohydride ($NaBH_4$) is being studied for chemical hydrogen storage and as an anodic fuel in fuel cells. This compound is stable for long periods of time in aqueous alkali solution (pH around 14) and presents no flammability hazards. Furthermore, sodium borohydride contains 10.5% hydrogen by mass, making it one of the most attractive media for hydrogen storage. In hydrogen storage applications, hydrogen is released through a hydrolysis reaction by contacting the solution with a heterogeneous catalyst (e.g. ruthenium) [1]:

$$NaBH_4 + 4H_2O \rightarrow NaB(OH)_4 + 4H_2 \quad (1)$$

When used as a direct fuel, the hypothetical oxidation reaction of sodium borohydride is:

$$BH_4^- + 8OH^- \rightarrow NaB(OH)_4 + 4H_2O + 8e^- \quad (2)$$

Note that if the oxidation of the hydrogen produced in Reaction (1) is considered, the two processes (borohydride as a source of hydrogen and as a direct fuel) are formally equivalent. The actual yield of electrons depends upon the anode material used [1]. The standard potential for the reverse of Reaction (2) [reduction of $B(OH)_4^-$ to BH_4^-] is −1.23 V vs. SHE.

Currently, sodium borohydride is too expensive to be widely used in automotive applications. There is interest in recycling the sodium metaborate ($NaB(OH)_4$) by-product from these reactions, for example by electrochemical reduction [2]. In fact, various boron oxides have been used; in this report, these will be referred to as *borates*. For tests of the early patents, the reader is referred to the work of Gyenge and Oloman [2]. Since their publication in 1998, new literature has been issued, again claiming the feasibility of this process.

Amendola was issued a patent in 2002 that includes aspects on electrochemical reduction of borates in aqueous solution [3]. This patent calls for the use of high overpotential cathodes, such as Bi, Tl, Cd, Sn, Pb, Ga, In, Hg, and amalgamated materials. In fact, this follows the direct reduction method tested by Gyenge and Oloman [2]. The anode material was suggested to be gold, iridium oxide, manganese (IV) oxide, or other materials that have a low overpotential for oxygen evolution, since the anode reaction is the oxidation of hydroxide ion to form oxygen. No examples of actual operation of the processes described in this patent were given by the authors.

Kawai and Ito were granted a patent in 2003 for production of alkali metal borohydrides in aqueous solution [4]. Materials suggested for the cathode include Ta, In, Zn, Pb, and C (hydrogen overpotential of more than 0.3 V preferably). Again, these cathode materials would promote the direct reduction pathway tested by Gyenge and Oloman [2]. A hydrogen gas-depolarized anode was suggested to minimize cell potential; thus anode materials having

* Corresponding author at: Center for Electrochemical Science and Technology, Department of Materials Science and Engineering, 201 Steidle Building, Pennsylvania State University, University Park, PA 16802, United States. Tel.: +1 814 863 7772; fax: +1 814 865 2917.
E-mail address: ddm2@psu.edu (D.D. Macdonald).

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a low potential for hydrogen oxidation were suggested as Pd, Pt, Ru, Os, Ir, Rh, etc. When using the hydrogen oxidation anode, avoiding co-evolution of oxygen is necessary for safety reasons, so materials having a large overpotential for hydroxide oxidation should be used. Several embodiments were given. The first of these examples called for a gas diffusion anode (for hydrogen oxidation), with H_2 supplied at a pressure of 0.2 MPa. The cathode was Ta and the cell divider was an anion-exchange membrane. The anolyte was 6 M NaOH and the catholyte was $NaBO_2$ in 6 M NaOH (concentration of $NaBO_2$ not given). A potential of 1 V was applied across the cell and a current efficiency of 80% was reported with respect to metaborate reduction. The analytical method used to establish the current efficiency was not disclosed. The use of an anion-exchange membrane is a mystifying choice; as such a membrane would allow any borohydride produced to eventually reach the anode where it would be destroyed.

Jianqiang et al. reported in a publication that reduction of $NaBO_2$ in aqueous, alkaline solution, could be accomplished at a copper cathode [5]. Many important details were missing in this report: the size and form of the cathode, the applied current, working electrode potential and/or cell potential, and the cell divider was reported to be a "self-made" cation-exchange membrane with no details given as to the constitution or preparation of this membrane. The authors did state that the anolyte was 1 M H_2SO_4 and the anode was Pb; the catholyte was 1 M NaOH with 0.2 M $NaBO_2$ and the cathode was copper. CV at a Cu working electrode (area and preparation not disclosed) at a sweep rate of 100 mV/s with a lead counter electrode and an SCE reference electrode was performed. A peak occurring at −1.52 V was supposed to be due to reduction of $NaBO_2$; the "drifting" of the "actual reduction potential" was supposed to occur due to adsorption and desorption of oxygen. Ion chromatography, X-ray diffraction (XRD), and iodometry (iodide back-titration method) were reported as analytical techniques.

In addition to the above sources, it has been pointed out to us that some more recent literature has been published suggesting that electrochemical reduction of borates is feasible [6,7]. However, as this literature was not available until after completion of the work described here, we were unable to evaluate these works in the laboratory.

One important aspect of borate reduction appears to have been overlooked by other workers is electrostatic repulsion of the borate anion from the cathode. Several ideas to overcome this problem were investigated by the present authors: (1) use of a cathode material having a very negative potential of zero charge (PZC) (Ti); (2) use of a rectangular wave pulse, a method already known in electroplating for such use [8]; (3) use of specifically adsorbable cations to modify the potential in the interfacial region; (4) modification of the cathode surface to promote attraction/binding of borate anions.

2. Experimental

The following metals were used as cathode materials: lead (99.9%), gold (99.95%), mercury (99.999%), titanium (99.99%), silver (99.9%), and copper (99.99%). All were obtained from Alfa Aesar. For all metals except for mercury, the cathodes took the form of a flag, 25 mm × 25 mm. A wire of the same metal as the cathode was attached to each flag, either by spot welding, or by drilling a hole in the top center of the flag, and hooking the wire through this hole. A piece of nickel or copper wire (except in the case of the copper electrode) was then soldered to the wire and the solder joint was protected by heat shrink PTFE tubing.

Graphite rod used as the anode was 6.3 mm diameter from Alfa Aesar (99% purity).

Electrolyte solutions were prepared from NaOH (EMD, 99% min), KOH (J.T. Baker, 88%), tetraethylammonium hydroxide (TEAH; Alfa Aesar, reagent grade, 35% (w/w) in water), tetramethylammonium hydroxide (TMAH; Alfa Aesar, 99.9999%, 25% (w/w) in water), tetrapropylammonium hydroxide (TPAH; Alfa Aesar, purity not specified). Distilled, de-ionized water from a Millipore system was used to prepare all solutions. Boric acid (J.T. Baker, ACS Reagent grade) and sodium metaborate tetrahydrate (Sigma–Aldrich, purity ≥99%) were used as starting materials. Sodium borohydride (Rohm and Haas Venpure granules) was kindly donated by Rohm and Haas.

For the solid metal electrodes, electrolyses were performed in an ESC C-600 glass cell. This cell is a basic H-cell, with ground glass joints for a reference electrode, gas sparging, electrodes, and other such fittings. A piece of Nafion 112, clamped between two expanded PTFE (Goretex®) gaskets and sealed with GE Silicon II, served as the cell divider for all experiments. In most experiments, the anolyte volume was 75–85 mL and the catholyte volume 30–40 mL at the start of the experiment. The counter electrode in these experiments was a Pt flag (25 mm × 25 mm^2). The cathodic current densities reported here are calculated based upon the apparent area of the front face of the cathode. For mercury pool cathode experiments, small, custom-made glass divided H-cells was used. As with the other cells, Nafion 112 cemented between Goretex gaskets was used as the divider. Electrical contact to the mercury pool was made through a stainless steel post. The inside diameter of the cathode compartment was 13 mm. The counter electrode was a 6.3 mm diameter graphite rod. Two different electrolytes "pairings" were used: *symmetrical*, meaning the anolyte and catholyte had the same composition, and *asymmetrical*, meaning the composition of the anolyte and catholyte differed. A particular case of the asymmetrical electrolyte was the use of 1 M H_2SO_4 for the anolyte. This was suggested by Jianqiang et al. [5]; as will be discussed later, electro-osmotic dilution of the catholyte appeared to be absent with this choice of catholyte. Some experiments utilized 1–3 mM $NaBH_4$ added to the catholyte, as a check on stability of $NaBH_4$ under electrolysis conditions.

Cyclic voltammetry, using a 6 mm diameter Au disk-working electrode, was used to test for the presence of borohydride in the catholyte solutions after electrolysis. This method is described elsewhere [9]. Briefly, a sweep rate of 100 mV/s over the range of −1 V to +0.3 was used; the counter electrode was a graphite rod, and the reference electrode was Hg/HgO in 2 M NaOH.

3. Results and discussion

3.1. Cathode materials: emphasis on metals with large overpotential for hydrogen evolution

The first approach in the electrolysis experiments focused on direct reductions with high overpotential cathodes. The reason for this is that many of the materials used as cathodes in direct reduction also happen to be good catalysts for hydrolysis of BH_4^-. As one example, Gyenge and Oloman reported that the Raney Ni bed caused rapid hydrogen evolution from an alkaline $NaBH_4$ solution [2]. Because hydrolysis of $NaBH_4$ had to be avoided, it appeared more profitable to focus on direct reductions for aqueous media.

Mercury is the quintessential high overpotential cathode material and is generally held to be the cathode material giving the most negative cathodic limit in aqueous solutions. However, and this was not appreciated early in this project, the formation of alkali metal amalgams is known to be the cathodic limit when alkali metal cations are present in solution [10]. For example, the standard potential for the deposition of sodium metal is −2.713 V (vs. standard hydrogen electrode, SHE). On the other hand, the potential for sodium deposition at a mercury cathode in 1 M NaOH has been reported to be −1.68 V (SHE; after conversion from the RHE scale) [11]. This potential is very far positive to the standard potential for