



Research Paper

The highly stable aqueous solution of sodium dodecahydro-*closo*-dodecaborate $\text{Na}_2\text{B}_{12}\text{H}_{12}$ as a potential liquid anodic fuel



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ABSTRACT

Herein are reported the first results and the discussion about the oxidation of the highly stable aqueous solution of sodium dodecahydro-*closo*-dodecaborate $\text{Na}_2\text{B}_{12}\text{H}_{12}$, a potential anodic fuel for energy conversion devices (fuel cells). The anion $\text{B}_{12}\text{H}_{12}^{2-}$ is indeed chemically stable: it has an excellent stability over 3 weeks in both alkaline and acidic media; and heterogeneous hydrolysis does not take place as evidenced by differential electrochemical mass spectrometry (DEMS) measurements (using a gold electrode). According to the cyclic voltammetry experiments, the $\text{B}_{12}\text{H}_{12}^{2-}$ anion can be oxidized over bulk electrodes made of platinum, gold or silver, the oxidation taking place at low potential values with platinum and high potential values with gold and silver electrodes. The overall reaction is complex and generates various products, which were analyzed over 1000 cycles of voltammetry in the range -1.05 and 0.6 V vs. SCE. These products are mainly composed of B- and B₁₁-based polyboranes, which is indicative of a partial oxidative degradation of $\text{B}_{12}\text{H}_{12}^{2-}$. To sum up, the present article demonstrates the potential of the aqueous solution of sodium dodecahydro-*closo*-dodecaborate $\text{Na}_2\text{B}_{12}\text{H}_{12}$ as anodic fuel, but it also stresses on the necessity of further works especially focusing on multi-metallic electrodes (electrocatalysts) that could quantitatively and completely valorize this fuel.

1. Introduction

Within the past two decades, boron hydrides have shown to be potential (i) materials for liquid- and/or solid-state chemical hydrogen storage and (ii) liquid anodic fuels of direct liquid fuel cells. Boron hydrides draw their strong potential from the hydridic hydrogen elements H^- . (i) They react with protic hydrogen atoms H^+ (e.g. from water) to generate H_2 ($\text{H}^- + \text{H}^+ \rightarrow \text{H}_2$), and (ii) they can be oxidized in alkaline medium with generation of 2 electrons ($\text{H}^- \rightarrow \text{H}^+ + 2e^-$) while the as-formed H^+ concomitantly react with OH^- towards the formation of H_2O . One can thus readily understand the potential of such hydrides in the field of new/alternative energies [1,2].

A first example of the aforementioned boron hydrides is sodium borohydride NaBH_4 . It has a good solubility in water (55 g in 100 g H_2O). It is not stable when the pH is below 7–8, due to the occurrence of self-hydrolysis ($\text{BH}_4^- + 4\text{H}_2\text{O} \rightarrow \text{B(OH)}_4^- + 4\text{H}_2$), but in alkaline conditions (pH = 9–12) the stability is drastically improved and can be considered near-perfect above pH = 13 [3–5]. Aqueous alkaline

solution of NaBH_4 is then suitable for the generation of electrons by (electrochemical) oxidation. The borohydride oxidation reaction (the so-called BOR: $\text{BH}_4^- + 8\text{OH}^- \rightarrow \text{BO}_2^- + 6\text{H}_2\text{O} + 8e^-$) was first reported in 1953 [6]. The standard potential of the reaction is -1.24 V vs. the reversible hydrogen electrode (RHE) [7], which is ca. 0.4 V below that for H_2 oxidation (pH = 14). This explains why in the past two decades, the borohydride oxidation reaction has been widely investigated for electrochemical energy conversion purposes [8–11] or for its interest as a strong reducing agent in metal deposition or chemical synthesis [12]. The following aspects, which are related to the main issues of using NaBH_4 as a strong reducer/fuel, have been especially investigated: electro-catalyst/catalysis of the BOR, features of the aqueous alkaline solution, membrane and crossover of ions, hydrolysis and oxidation mechanisms, and cathode (fuel and electrocatalyst) (see e.g. [11] for details).

A second example of boron hydride is the adduct ammonia borane NH_3BH_3 . It is soluble in water (35 g in 100 g H_2O) and satisfactorily stable when the pH is 7 or above [13]. Within the past two decades, the

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oxidation of this compound ($\text{NH}_3\text{BH}_3 + 6\text{OH}^- \rightarrow \text{NH}_4^+ + \text{BO}_2^- + 4\text{H}_2\text{O} + 6\text{e}^-$; standard potential of -1.22 V vs. RHE) has been scarcely studied [14–19]. In fact, NH_3BH_3 and NaBH_4 suffer from the same main issues (e.g. the occurrence of heterogeneous hydrolysis with evolution of the unwanted H_2). However, NaBH_4 is superior in terms of theoretical (and usually also of effective) number of electrons exchanged (6 vs. 8 respectively), and NH_3BH_3 is synthesized from NaBH_4 making it more expensive [20]; both points explain why the development of aqueous NH_3BH_3 as liquid anodic fuel remains limited in comparison to NaBH_4 .

More recently, a third example of boron hydride, sodium octahydro-ditriborate NaB_3H_8 , has been reported [21]. It is much soluble in water (74 g in 100 g H_2O), even more soluble than NaBH_4 , but the aqueous solution of NaB_3H_8 is comparable to the aqueous solution of NaBH_4 in terms of stability even in alkaline conditions. In solution, the B_3H_8^- anion transforms into the BH_4^- anion and the latter readily hydrolyzes. Regardless of that, NaB_3H_8 is a possible liquid anodic fuel. Theoretically, the oxidation is expected to release 18 electrons ($\text{B}_3\text{H}_8^- + 20\text{OH}^- \rightarrow 3\text{BO}_2^- + 14\text{H}_2\text{O} + 18\text{e}^-$; standard potential of the reaction not available). Experimentally, the effective number of electrons is 10 electrons with a gold electrode, the authors pointing out that gold may not be the proper electrocatalyst to valorize B_3H_8^- . Incomplete oxidation is due to the occurrence of heterogeneous hydrolysis (and H_2 evolution).

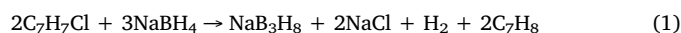
As mentioned above, the oxidations of NaBH_4 , NH_3BH_3 and NaB_3H_8 suffer from several problems relating to the aqueous solution properties, the electrocatalyst (nature and texture), the membrane and so forth. Two aspects are particularly problematic: the instability of the boron hydride in water (mainly in the case of NaBH_4 and NaB_3H_8) and the nature of the borate by-product (BO_2^- for the anhydrous form and the $\text{B}(\text{OH})_4^-$ for the hydrated compound). The former issue has been briefly discussed in the previous paragraphs. The latter issue is inherent to the high stability of the B–O bonds, which is comparable to that of the C=O bonds in carbon dioxide CO_2 . The recycling of BO_2^- with regeneration of NaBH_4 is thermodynamically unfavorable and currently realized through costly processes [22]. Yet, it is pivotal to close the energy cycle with boron hydrides for a possible near-future technological deployment. Breakthrough in the recycling of borates is evidently required.

Another strategy would be to circumnavigate the aforementioned challenges by envisaging alternative liquid anodic fuels, and it was chosen to explore this strategy. The chemistry of boranes has a history going back one century: it has given rise to a very great number of molecules, from diborane B_2H_6 to polyhedral boranes. Polyhedral boranes have been widely used in medical and pharmacological applications owing to their exceptional stability (low chemical reactivity and resistance to breakdown in biological systems) rendering them relatively nontoxic [23,24]. For the present work, a polyhedral borane anion salt, namely sodium dodecahydro-closo-dodecaborane $\text{Na}_2\text{B}_{12}\text{H}_{12}$, was selected. It has a good solubility in water, is stable in aqueous solution, is comparable to sodium chloride NaCl in terms of nontoxicity, and is less sensitive to catalytic hydrolysis than other polyhedral borane anions like $\text{B}_{10}\text{H}_{10}^{2-}$ and $\text{B}_{11}\text{H}_{14}^-$ [24,25]. Accordingly, is reported herein, for the first time, preliminary results about the oxidation of aqueous $\text{Na}_2\text{B}_{12}\text{H}_{12}$ on bulk electrodes (platinum, gold, or silver) as well as a discussion about its potential as liquid anodic fuel.

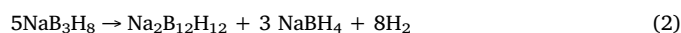
2. Experimental

The synthesis of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ was performed according to a new multi-step procedure, actually adapted from previous reports [26,27]. The manipulations were performed under argon. Standard Schlenk-line and glove box (MBraun M200B; $\text{O}_2 < 0.1\text{ ppm}$; $\text{H}_2\text{O} < 0.1\text{ ppm}$) techniques were used. In a three-necked round-bottom flask equipped with a condenser, 20 g of NaBH_4 ($\geq 98\%$, Sigma-Aldrich) were

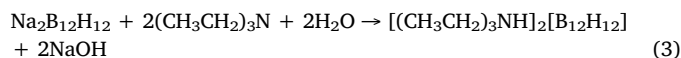
dispersed in 350 mL anhydrous diglyme $\text{C}_6\text{H}_{14}\text{O}_3$ ($\geq 99\%$, Sigma-Aldrich) and heated up to $100\text{ }^\circ\text{C}$. Using an addition funnel, 50 mL of benzyl chloride $\text{C}_7\text{H}_7\text{Cl}$ ($\geq 99\%$, Sigma-Aldrich) was slowly added to the NaBH_4 dispersion. NaB_3H_8 formed (^{11}B NMR (96.29 MHz, CD_3CN) $\delta -30.6\text{ ppm}$ (nonet); ^1H NMR (300.13 MHz, CD_3CN): $\delta 0.2\text{ ppm}$ (decet)) [21]:



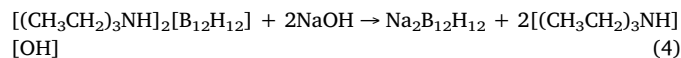
Upon the completion of this reaction, the temperature was increased to $165\text{ }^\circ\text{C}$. NaB_3H_8 decomposed:



The reaction mixture was kept at $165\text{ }^\circ\text{C}$ overnight. Then, the solvent was extracted at $140\text{ }^\circ\text{C}$ under vacuum. The setup was cooled down to room temperature and the drying was completed under dynamic vacuum at $-47\text{ }^\circ\text{C}$. A yellowish solid consisting of mainly $\text{Na}_2\text{B}_{12}\text{H}_{12}$ and NaBH_4 was obtained. For purification, the solid was dissolved in 150 mL of Milli-Q water (18.2 M Ω cm) and 60 mL of hydrochloric acid HCl (36.5–38%, Sigma-Aldrich). The additions were done very slowly because of the evolution of H_2 by acid attack of NaBH_4 ($\text{Na}_2\text{B}_{12}\text{H}_{12}$ is stable in acidic medium). Boric acid $\text{B}(\text{OH})_3$ formed. It was crystallized by storing the solution at $-6\text{ }^\circ\text{C}$ overnight. The as-formed crystals were filtrated. Then, about 50 mL of triethylamine $(\text{CH}_3\text{CH}_2)_3\text{N}$ ($\geq 99\%$, Sigma-Aldrich) was added to the acidic aqueous solution to increase the pH up to 9–10. The as-obtained alkaline solution was stirred overnight. A white precipitate formed:



It was collected by filtration and dried under dynamic vacuum at ambient temperature. The remaining traces of boric acid were removed by dissolution with 50 mL of Milli-Q water at $60\text{ }^\circ\text{C}$. Purified $[(\text{CH}_3\text{CH}_2)_3\text{NH}]_2[\text{B}_{12}\text{H}_{12}]$ was recovered after filtration. As a last step, cation substitution was performed by interaction with sodium hydroxide NaOH ($\geq 98\%$, BioXtra) in Milli-Q water:



By this way, 3.6 g of a white solid consisting of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ was recovered (yield of 43.5%).

Nuclear magnetic resonance (NMR) was used for the structural analysis of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ in solution: nuclei ^1H and ^{13}C (probe head dual $^1\text{H}/^{13}\text{C}$, 300.13 MHz, CD_3CN , $30\text{ }^\circ\text{C}$); nucleus $^{11}\text{B}\{^1\text{H}\}$ (probe head BBO10, 96.29 MHz, D_2O , $30\text{ }^\circ\text{C}$); apparatus Bruker AVANCE-300. Analyses by Fourier transform infrared (FTIR; Nicolet 710, 128 scans) and Raman spectroscopy techniques were also performed. For the latter technique, the measurements were carried out using a confocal micro-spectrometer (Labram HR, Jobin-Yvon) with the sample in a sealed glass tube kept at $25\text{ }^\circ\text{C}$ (diode laser beam 659.55 nm). Powder X-ray diffraction (PXRD) was carried out on a PANalytical X'Pert diffractometer equipped with an X'Celerator detector. The 2θ range was between 10 and 50° . Pattern matching was performed using the EVA software and available crystallographic databases (PDF-4 + v. 4.1403). Thermogravimetric analysis (TGA) of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ was performed with the apparatus TGA Q500 of TA Instruments. Typically, $\sim 3\text{ mg}$ of solid was introduced into an aluminum crucible (40 μL) and then heated up to $400\text{ }^\circ\text{C}$ at 5 min^{-1} under N_2 flow (60 mL min^{-1}). The same experimental conditions were applied for analysis by differential scanning calorimetry (DSC; apparatus: 2920 MDSC of TA Instruments).

Cyclic voltammetry (CV) experiments were performed with a $\mu\text{Autolab}^\circ$ Type III potentiostat using a three-electrode cell. Saturated calomel electrode (SCE, the reference potential of which is 0.241 V vs. SHE, i.e. 1.008 V vs. RHE, pH = 13) was used as reference electrode and platinum wire as counter electrode. Gold ($\phi 1\text{ mm}$), platinum ($\phi 1\text{ mm}$), silver ($\phi 2\text{ mm}$) and glassy carbon ($\phi 2\text{ mm}$) were used as

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