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Assessing the Potential of Sodium 1-Oxa-\textit{nido}-dodecaborate NaB_{11}H_{12}O for Energy Storage

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ABSTRACT: In the recent years, polyborate anions have been considered as possible candidates for energy. In aqueous solutions, they have been studied as either hydrogen carriers or anodic fuels. In the solid state (as an alkali salt), they have been seen as solid electrolytes. Herein, we focus on sodium 1-oxa-\textit{nido}-dodecaborate NaB_{11}H_{12}O, a novel possible candidate for the aforementioned applications. The compound is soluble in water, and its stability depends on pH: under acidic conditions, it readily hydrolyzes while liberating hydrogen, and under alkaline conditions, it is stable, which is a feature searched for an anodic fuel. Over bulk platinum, gold, or silver electrode, oxidation takes place. The best performance has been noticed for the silver electrode. In the solid state, NaB_{11}H_{12}O shows Na^+ conductivity at a high temperature of up to 150 °C. All of these properties are presented in detail, and hereafter they are discussed while giving indications of what have to be developed to open up more realistic perspectives for NaB_{11}H_{12}O in energy.

1. INTRODUCTION

Carbon as the main element of fossil fuels has played a central role over the past decades. Nowadays, things are changing and alternative energy sources and carriers are being taken into the 21st century. Carbon will still play a role in the field but any fuel like formic acid and liquid organic carriers will be renewable in order to get closed carbon cycles.1–3 Search for alternative energy solutions has opened opportunities for compounds made of other elements. Owing to its position in the periodic table against carbon, boron was innately envisaged and, as a matter of fact, boron-based materials have been much investigated since the early 2000s.4–6

Boron-based materials have been first seen as liquid-state and solid-state hydrogen carriers. Typical examples are sodium borohydride (NaBH$_4$) and ammonia borane (NH$_3$BH$_3$). The former is mainly considered in aqueous solutions in such a way that the couple NaBH$_4$−4H$_2$O has a maximum gravimetric hydrogen capacity of 7.3 wt % (if the catalyst weight is not taken into account) and the stored hydrogen is released by catalytic hydrolysis.7 The latter material has also been considered in aqueous solutions for hydrolytic dehydrogenation.8 However, it is more attractive for solid-state hydrogen storage where most of the stored hydrogen (13 wt %) is generated by thermolytic dehydrocoupling.9 Many other boron-based materials (most being derivatives of NaBH$_4$ and NH$_3$BH$_3$) emerged as possible candidates for hydrogen storage.4–6 One may cite as uncommon examples the polyborate anions such as nido-B$_{11}$H$_{14}^-$, closo-B$_{10}H$_{10}^{2−}$, and closo-B$_{12}H$_{12}^{2−}$; they may be hydrolyzed in the presence of a rhodium-based catalyst at 80 °C.10

Boron-based materials like the aforementioned NaBH$_4$ and NH$_3$BH$_3$ are reducing agents. They (as alkaline aqueous solutions) can therefore be used as anodic liquid fuels of direct liquid-fed fuel cells. The former has been much more investigated owing to a higher theoretical specific energy and a lower cost.11 Yet, the development of the direct borohydride fuel cell is impeded by technical issues, one of them being the “unwanted” heterogeneous hydrolysis of NaBH$_4$ (then, in competition with the expected oxidation).12 This prompted us to explore the potential of more stable boron-based materials. We first considered the aqueous solution of sodium octahydrotriborate (Na$_3$B$_8$H$_8$) but, like for NaBH$_4$, heterogeneous hydrolysis took place in some extent. Accordingly, oxidation of B$_{12}$H$_{12}^-$ on platinum and gold electrodes was found to generate effective numbers of electrons of about 5 and 10 out of a theoretical total of 18 electrons.13 We secondly considered oxidation of the highly stable aqueous solution of sodium dodecahydro-closo-dodecaborate (Na$_2$B$_{12}$H$_{12}$). It was found to partially oxidize over bulk electrodes (platinum, gold or silver), and much attractively, heterogeneous hydrolysis does not occur.14

Boron-based materials have also shown to be potential electrolytic materials of all solid-state Li- or Na-ion batteries. A first example is lithium borohydride (LiBH$_4$). Its hexagonal P6$_3$/mmc phase, forming at about 110 °C, was found to have a high

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electrical conductivity of the order of \( mS \ cm^{-1} \). High \( Li^+ \) conductivity (0.1 \( mS \ cm^{-1} \)) can be achieved at room temperature by confining borohydride in the pores of nanoporous silica. A second example of the boron-based electrolyte is \( Na_2B_{12}H_{12} \). The \( Na^+ \) conductivity was measured as 100 \( mS \ cm^{-1} \) at 256 °C. Appreciable ionic conductivity (0.5 \( mS \ cm^{-1} \)) was achieved under room conditions for a derivative, \( Na_3(BH_4)_{(B_{12}H_{12})} \), made of borohydride and dodecahydro-closo-dodecaborate anions. With such performance, a number of new compounds, most being the derivatives of the aforementioned materials, have been developed.

If the situation is briefly redescribed, it is arguable that boron-based materials have shown to be compounds with prospectives in three energy applications: namely, chemical hydrogen storage, energy storage, and energy conversion.
storage, anodic fuel of the direct liquid-fed fuel cell, and solid electrolyte of the all-solid battery. Of the materials investigated so far, alkali polyborates have recently emerged and there is a growing interest in them. The present work is viewed in this context. We initially focused on the synthesis of sodium tetradecahydro-rido-undecaborate NaB₁₁H₁₄ but because it is unstable in the basic medium, we finally focused on the forming derivative, that is, sodium 1-oxa-undecahydro-rido-dodecaborate NaB₁₁H₁₂O. The compound was properly characterized and its properties related to the aforementioned applications were assessed. The results that are presented herein allow us to position NaB₁₁H₁₂O in the field of energy storage.

2. RESULTS AND DISCUSSION

2.1. Toward NaB₁₁H₁₂O. Our preliminary objective was the synthesis of the cluster NaB₁₁H₁₄. It was synthesized according to a stepwise process involving NaBH₄ as the starting material.²⁰⁻²¹ The ¹¹B NMR spectrum (Figure 1a) is in good agreement with a previously reported one,²² confirming the successful synthesis of the pure compound. It is worth mentioning the absence of peaks at δ > 0 ppm, discarding the presence of any other B bond-containing product. The signal of highest intensity at 2.3 ppm is attributed to water and the intensity is higher than that of CH₃CN of the anhydrous deuterated solvent (δ = 2.3 ppm). A last analysis of the sample was performed by Fourier transform infrared spectroscopy (FTIR) (Figure 1c). The fingerprint is typical of a compound made of B–B and B–H bonds. The presence of H₂O is confirmed by, for example, the bands at 3800–3200 cm⁻¹ (O–H stretching). It is therefore reasonable to attribute these signals to H₂O molecules, complexing the cluster NaB₁₁H₁₄.

For a use as the anodic fuel of the direct liquid-fed fuel cell, NaB₁₁H₁₄ is expected to be stable in aqueous alkaline solution (NaOH 0.1 M). A solution was prepared (to be stored in an argon-filled glovebox) and the stability was followed by ¹¹B NMR. After 2 h, several new signals at δ < −17 ppm and δ > −10 ppm were observed (Figure 1d), suggesting an evolution of NaB₁₁H₁₄ in alkaline solutions. The instability of the anion B₁₁H₁₂O⁻ in aqueous alkaline solutions was reported elsewhere: Ouaassas et al. observed the formation of the 1-oxa-undecahydro-rido-dodecaborate anion (B₁₁H₁₂O⁻) by reaction of O₂ with an alkaline solution of B₁₁H₁₄.²³ Hence, in our conditions, we waited for the complete oxidation of NaB₁₁H₁₄. The process took 21 days for a vial stored in the glovebox at room temperature.

The ¹¹B NMR spectrum of the as-formed compound is shown in Figure 2a. It is in good agreement with the molecular structure of the anion B₁₁H₁₂O⁻.²³ The FTIR spectrum of the oxidation product (Figure 2b) is comparable to that of NaB₁₁H₁₄ with the presence of the typical bands for the B–B, B–H, and O–H bonds. There are also small differences that are because of the presence of the B–O bond. NMR analysis of the nucleus²⁵Na was performed (Figure 2c). The spectrum is featured by only one signal at δ = −7.5 ppm. This is in good agreement with a cation Na⁺, compensating the negative charge of an inorganic anion.²⁵ As a last analysis, the molecular weight of the product was determined by mass spectrometry (Figure 2d). An m/z value of 146.8 was found. It is comparable to the molecular weight of B₁₁H₁₂O⁻ (147 g mol⁻¹), knowing besides that the isotopic pattern score correlates with this anion. Another signal at m/z 126.5 was noted. It is ascribed to B₁₁H₁₃, which could be produced by fragmentation of the parent anion during the analysis. To sum up, all of the analyses reported above confirm the complete oxidation of NaB₁₁H₁₄ into NaB₁₁H₁₂O when kept in alkaline solution for 21 days.

NaB₁₁H₁₂O is a white solid. It is crystalline. Its X-ray diffraction (XRD) pattern is reported herein for the first time (Figure 3). Using the pattern matching based on the PAnalytical X’Pert HighScore software and the available crystallographic databases (PDF-4+ v. 4.1403), no matching was found for a screening using the constitutive elements Na, B, O, and H. An extended search including the elements present in the initial reactant revealed traces of both NaCl (ref. pattern 00-001-0993) and NaOH-H₂O (ref. pattern 00-002-0706). These observations suggest that the compound is a new crystalline phase. A work is in progress to obtain a sample with a better crystallinity and/or a monocrystal to solve the crystal structure and propose a set of cell parameters.

2.2. Hydrolytic Stability of NaB₁₁H₁₂O. The stability of NaB₁₁H₁₂O in aqueous solutions was verified. Though formed in alkaline solution (NaOH 0.1 M), a further test was performed for a higher NaOH concentration. The solid was dissolved in a solution at 1 M NaOH to get a concentration of 10⁻⁵ M and the as-prepared solution was stored for 25 days under an argon atmosphere (in the glovebox) and at room temperature. No evolution was observed (Figure 4), allowing to go further with this compound as the anodic fuel, that is, for oxidation over bulk metal electrodes.

The stability in the acidic medium was also envisaged. A solution of H₂SO₄ (0.1 M) was prepared. It was used to dissolve NaB₁₁H₁₂O. Polyborate anions like B₁₀H₁₀⁻ and B₁₁H₁₁⁻ are known to be stable in the acidic medium.²⁶⁻²⁸ In contrast, anions like B₁₁H₁₂²⁻, B₁₁H₁₄⁻, and B₁₂H₁₄²⁻ are hydrolytically unstable in the acidic medium.²⁵⁻²⁸ In our conditions, NaB₁₁H₁₂O reacted violently in the acidic medium. The reaction was characterized by immediate gas formation: hydrolysis with generation of hydrogen took place. Like, for example, nido-B₁₁H₁₄⁻ could open prospectives for chemical hydrogen storage because NaB₁₁H₁₂O carries 6.7 wt % of hydrogen.

2.3. Oxidability of NaB₁₁H₁₂O. The stability of NaB₁₁H₁₂O in alkaline solutions is a required property for an anodic fuel. To the authors’ knowledge, oxidation of such a compound has not
been reported before. The discussion below is thus based on the literature dedicated to NaBH₄, NaB₃H₈, and NaB₁₂H₁₂.

The oxidation of NaB₁₁H₁₂O was first studied by cyclic voltammetry (CV) with bulk platinum as the electrode and under natural diffusion conditions (Figure 5a). The concentration of NaOH was set at 0.1 M and the concentration of the sample at 0.001 M. The voltammogram resembles that recorded for NaB₁₂H₁₂ with the same electrode. For the forward scan, there are two oxidation peaks. They are in the region of adsorption/desorption of atomic hydrogen on the electrode surface: aPt₁ at −0.73 V versus the saturated calomel electrode (SCE) and aPt₂ at −0.6 V versus SCE. Dissociative adsorption of B₁₁H₁₂O⁻ followed by oxidation of the adsorbed hydrogen H₄ads would happen. Direct partial oxidation of the anion is also likely to happen. At higher potential, in the region of platinum oxides, there is no oxidation peak, maybe because of electrode poisoning by adsorption of polyborate intermediates or desorption of the same species. For the backward scan, there is one oxidation peak (cPt₁) at −0.69 V versus SCE. It is attributed to the probable oxidation of H₄ads. The recorded current densities are very low (<2 mA cm⁻² for e.g. aPt₁).

Oxidation of B₁₁H₁₂O⁻ over the platinum electrode seems to be tough, which might be explained by difficult dissociation of B₁₁H₂O²⁻ on the metal surface and/or the absence of direct oxidation. Additional CV experiments were performed with different rotation rates of the platinum rotating electrode (Figure 5b). The oxidation waves were confirmed and the voltammograms were compared to that recorded under natural diffusion conditions. The current densities slightly increased with the increase of the rotation rate. This may be explained by desorption of polyborate intermediates.

The oxidation of NaB₁₁H₁₂O was then studied by CV with bulk gold as the electrode and under natural diffusion conditions (Figure 6a). The voltammogram shows one oxidation peak at +0.22 V versus SCE (aAu₁) during the forward scan and another one at +0.02 V versus SCE (aAu₂) during the backward scan. The oxidations are irreversible. They may be ascribed to direct oxidation of B₁₁H₁₂O⁻ or oxidation of intermediates. The current density of aAu₁ (3.4 mV cm⁻²) is slightly higher than that of aPt₁ but the oxidation takes place at too positive potential, which makes it less attractive. Gold does not generate current below −0.2 V versus SCE. It would be unable to valorize possibly formed H₄ads species. The rotation of the electrode (Figure 6b) has a positive effect. The current density for aAu₁ increases up to 7 mV cm⁻² at 2500 rpm. Gold is thus less impacted by poisoning from adsorbed polyborate intermediates than platinum is.

The oxidation of NaB₁₁H₁₂O was finally studied by CV with bulk silver as the electrode and under natural diffusion conditions (Figure 7a). The forward scan is characterized by two oxidation waves: aAg₁ at +0.16 V versus SCE and aAg₂ at +0.46 V versus SCE. Direct oxidation of B₁₁H₂O²⁻ and/or oxidation of intermediates seems to occur, oxidation being promoted by the formation of surface (hydr)oxides. The
backward scan is featured by one reduction peak (cAg2) at +0.1 V versus SCE. It implies that the oxidation process is, at least in part, reversible. The current densities are higher than those measured with the gold and platinum electrodes. For example, the value is 15.5 mA cm$^{-2}$ for aAg2. Direct and potentially more complete oxidation of B$_{11}$H$_{12}$O$^-$ is feasible on silver. At different rotation rates of the rotating silver electrode (Figure 7b), the aforementioned oxidation and reduction processes were confirmed. The current densities were found to slightly increase with, for example, 21.3 mA cm$^{-2}$ at 2500 rpm for aAg2. This suggests that the electrode would be less impacted by surface poisoning caused by adsorbed oxidation/reduction intermediates.

The best electrode is bulk silver when the electrochemical activity (i.e., current density) is considered only. Oxidation takes place at high potential; this is not really attractive for an anodic fuel. From a fundamental point of view, this shows that oxidation occurs in the metal-oxide region. Like for the anion B$_{12}$H$_{12}^-$, these results demonstrate the critical role of surface (hydr)-oxides in direct oxidation of B$_{11}$H$_{12}$O$^-$. The challenge would then be to develop multimetallic silver-based catalysts showing decreased oxidation potentials. If B$_{11}$H$_{12}$O$^-$ is compared to the anion B$_{12}$H$_{12}^-$, it has a lower electrochemical activity.

The oxidation products were qualitatively analyzed by mass spectrometry. Additional CV experiments were performed for each electrode: 1000 cycles where the potential was positively scanned from 1.05 to +0.6 V versus SCE (no reverse scan) were realized. A fraction of the electrolyte (1 mL) was collected every 100 cycles for analysis. The analyzed fractions revealed the presence of several m/z values, indicating then a complex composition. The possible species corresponding to these values were tentatively denoted on the basis of the available literature. The results are summarized in Table 1. For the platinum electrode, six different species were detected but the predominant one is B$_{11}$H$_{12}$O$^-$, which presumably forms by oxidation of one of the H of B$_{11}$H$_{12}$O$^-$. Oxidation of B$_{11}$H$_{12}$O$^-$ with OH$^-$ yields B$_{11}$H$_{10}$O$^-$ as the predominant product, 

$$B_{11}H_{12}O^- + OH^- \rightarrow B_{11}H_{10}O^- + H_2O + 2e^- \quad (1)$$

Partial oxidative degradation is a minor path for this electrode. The product identification allows better understanding of the low electrochemical activity of platinum, which would be mainly associated to oxidation of H$_{ad}$. With respect to the gold and silver electrodes, less and different species are formed. Three were detected and identified: B$_{11}$H$_{10}$O$^-$, B$_{11}$H$_{9}$O$^-$, and B$_{11}$H$_{8}$O$^-$. The formation of the most abundant product B$_{11}$H$_{10}$O$^-$ may be proposed to take place as follows

$$B_{11}H_{12}O^- + 140H^+ \rightarrow B_{11}H_{10}O^- + 3B(OH)_4^- + 2H_2O + 11e^- \quad (2)$$

Some partial oxidative degradation of B$_{11}$H$_{12}$O$^-$ occurred on gold and silver. These observations are in agreement with the CV results obtained with the three electrodes (Figures 5–7).

### 2.4. Ionic Conductivity of NaB$_{11}$H$_{12}$O

Recently Duchêne et al. reported a stable 3 V sodium-ion battery based on the use of a solid-state mixed polyborate, namely Na$_2$(B$_{12}$H$_{12}$)$_{0.5}$(B$_{10}$H$_{10}$)$_{0.5}$, as the electrolyte. The use of this material was motivated by an excellent thermal stability up to 300 °C and a high Na$^+$ conductivity of 0.9 mS cm$^{-1}$ at 20 °C. This is a promising achievement that follows one of the first works about the use of thermally and (electro)chemically stable sodium polyanions (e.g., Na$_2$B$_{12}$H$_{12}$) as potential solid-state electrolytes.

We measured ionic conductivities of NaB$_{11}$H$_{12}$O by using a broadband impedance spectrometer in a range of frequency varying from 0.01 Hz and 1 MHz, with an applied ac voltage of 1 V, and for temperatures from 150 to 0 °C. The results are shown in Figure 8a. Typically, the real part of the ac conductivity, $\sigma(\omega, T)$, results from the combination of three contributions

$$\sigma(\omega, T) = \sigma_{WVS}(\omega, T) + \sigma_{dc}(T) + \sigma'(\omega, T) \quad (3)$$

The polarization component $\sigma'(\omega, T)$, corresponding to the increasing part of the signal observed at high frequency, arises from the local rearrangement of the Na$^+$ charges causing dipolar reorientation. It is preponderant in the electrical response recorded in the lower temperature domain. The dc conductivity plateau $\sigma_{dc}(T)$, resulting from the long-range redistribution of the Na$^+$ ions, dominates the intermediate frequency region. Its contribution increases with the temperature, in agreement with a
thermally activated process. The Maxwell Wagner Sillars contribution \( \sigma_{MW}(\omega, T) \), corresponding to the signal decrease at a low frequency, is only observed for data recorded at high temperatures. It is because of the charge accumulation at the sample/electrode interface and actually supports the ionic features of the charge carriers. Compared to Na\(_3\)B\(_{12}\)H\(_{12}\), the conductivity performances of NaB\(_{11}\)H\(_{12}\)O are comparable (\( \sigma < 10^{-8} \text{ S cm}^{-1} \) at \( T > 150 \, ^\circ\text{C} \)). However, unlike other sodium polyborates (e.g. NaB\(_{11}\)H\(_{14}\) with \( \sigma \) between \( 10^{-2} \) and \( 10^{-1} \) S cm\(^{-1} \) at \( 90-160 \, ^\circ\text{C} \), and NaB\(_{12}\)H\(_{10}\) with ca. \( 8 \times 10^{-2} \) S cm\(^{-1} \) at \( 150 \, ^\circ\text{C} \)),\(^{41,42}\) the conductivity performances of NaB\(_{11}\)H\(_{12}\)O are quite low in relation with a lower density and/or lower mobility of the charge carrier Na\(^+\). Though the current performances are below the state of the art, there is a room for improvements for NaB\(_{11}\)H\(_{12}\)O, especially by focusing on the research avenues mentioned above.

In conclusion, the hydrolytic, oxidation, and conductivity properties of NaB\(_{11}\)H\(_{12}\)O have been investigated. It stands out that the compound is not stable in the acidic medium, it is stable in the alkaline medium, it is rather stable toward oxidation (over Pt, Au, and Ag electrodes) in the alkaline medium, and it shows low mobility of the charge carrier Na\(^+\). Though the current performances are below the state of the art, there is a room for improvements for NaB\(_{11}\)H\(_{12}\)O, especially by focusing on the research avenues mentioned above.

4. MATERIALS AND METHODS

The synthesis of NaB\(_{11}\)H\(_{14}\) was adapted from a protocol reported elsewhere.\(^{20,21}\) In an argon-filled glovebox (MBraun M200B, O\(_2\) <0.1 ppm, H\(_2\)O <0.1 ppm), 15 g of NaBH\(_4\) (Sigma-Aldrich) and 100 mL of anhydrous diglyme (Sigma-Aldrich) were transferred into a three-necked round-bottom Schlenk flask. The flask was connected to a vacuum-argon line, a refrigerant, and an addition funnel containing 63 mL of boron trifluoride diethyl etherate BF\(_3\)·O(C\(_2\)H\(_5\))\(_2\) (Sigma-Aldrich). The slurry was heated up to 105 \(^\circ\text{C}\). The reactant BF\(_3\)·O(C\(_2\)H\(_5\))\(_2\) was added dropwise over a period of 6 h. A yellow precipitate was formed

\[
17\text{NaBH}_4 (s) + 20\text{BF}_3\cdot\text{O(C}_2\text{H}_5)_2 (l) \\
\rightarrow 2\text{NaB}_3\text{H}_{14} (s) + 15\text{NaBF}_4 (s) + 20\text{H}_2 (g) \\
+ 20\text{O(C}_2\text{H}_5)_2 (l)
\]

The precipitate was filtered and heated at 80 \(^\circ\text{C}\) to evaporate most of the solvent. Because of residual diglyme and impurities, an aqueous solution (1.31 M) of trimethylamine hydrochloride (CH\(_3\)\(_3\)NHCl (Sigma-Aldrich)) was added onto the precipitate

\[
\text{NaB}_3\text{H}_{14} (s) + (\text{CH}_3)_3\text{NHCl (l)} \\
\rightarrow (\text{CH}_3)_3\text{NB}_{12}\text{H}_{14} (s) + \text{NaCl (aq)}
\]

Most of the impurities were dissolved in water, whereas the intermediate (CH\(_3\)\(_3\)NH)\(_3\)NB\(_{12}\)H\(_{14}\) (s) was in the form of a yellow precipitate. A last purification was done by washing with acetone C\(_3\)H\(_6\)O (Sigma-Aldrich), followed by addition of water at 57 \(^\circ\text{C}\) (boiling temperature of acetone). Owing to the miscibility of acetone in water and the insolubility of (CH\(_3\)\(_3\)N)\(_3\)NB\(_{12}\)H\(_{14}\), a pure
compound was recovered by filtration and drying under vacuum. As a final step, \((\text{CH}_3)_2\text{NHB}_1\text{H}_{14}\) (1 g) was reacted with an aqueous solution of \(\text{NaOH} (0.208 \text{ g})\) at \(80 \degree \text{C}\) for 2 h. Cation substitution took place

\[
(\text{CH}_3)_2\text{NHB}_1\text{H}_{14} (s) + \text{Na}^+ (aq) \\
\rightarrow \text{NaB}_1\text{H}_{14} (s) + (\text{CH}_3)_2\text{NH}^+ (aq)
\]

(7)

The yield was found to be 80%. The purity was 99%. \(\text{NaB}_1\text{H}_{14}\) was not stable in alkaline aqueous solution (\(\text{NaOH} 0.1 \text{ M}\)). It evolved into a new product, which was found to be \(\text{NaB}_1\text{H}_{12}\text{O}\). A complete oxidation of \(\text{NaB}_1\text{H}_{14}\) into \(\text{NaB}_1\text{H}_{12}\text{O}\) took 21 days under an argon atmosphere.

The polyborate anions in aqueous solution were analyzed by nuclear magnetic resonance (NMR) on Bruker AVANCE-300: \(^1\text{H}\) (probe head dual \(^1\text{H}/^{13}\text{C}, 300.13 \text{ MHz}, \text{CD}_2\text{CN}, 30 \degree \text{C})

\(^{11}\text{B}\), and \(^{23}\text{Na}\) (probe head BBO10, 96.29 and 79.39 MHz, \(\text{D}_2\text{O}, 30 \degree \text{C}\)). In the solid state, \(\text{NaB}_1\text{H}_{14}\) and \(\text{NaB}_1\text{H}_{12}\text{O}\) were analyzed by FTIR (Nicolet iS50 Thermo Fisher Scientific; 128 scans). The crystallinity of \(\text{NaB}_1\text{H}_{12}\text{O}\) was verified by powder XRD. The experiment was performed on a PANalytical X’Pert diffractometer equipped with an X’Celerator detector. The diffraction pattern was recorded using a monochromatic wavelength (\(\text{Cu K}_{\alpha}, \lambda = 1.540593 \text{ Å}\)) in the 2\(\theta\) range 5\(^{\circ}\)–100\(^{\circ}\) with an operating voltage of 40 kV and a beam current of 40 mA using 40 kV. The sample in the powder form was placed into a glass capillary (1 mm diameter) sealed to prevent any decomposition under moisture of ambient air.

Oxidation of \(\text{NaB}_1\text{H}_{12}\text{O}\) was studied by CV using a \(\mu\)Autolab Type III potentiostat using a three-electrode cell. SCE was used as the reference electrode. The platinum wire was used as the counter electrode. Platinum (Ø 2 mm) or gold (Ø 2 mm) or silver (Ø 4 mm) was used as the rotating disk working electrode. Outgassed Milli-Q Water (18.2 \(\Omega\) cm, <3 ppb total organic carbon) was used. For any new measurement, the glassware and electrodes were treated with peroxymonosulfuric acid \(\text{H}_2\text{SO}_8\) (Caro’s acid) overnight and carefully washed with Milli-Q water; then the working electrode surfaces were polished with diamond paste. The cell, thermostatted at 20 \degree \text{C}, was degassed with argon. In doing oxygen reduction and carbonation of the electrolyte from ambient carbon dioxide was avoided. In order to avoid water splitting, the voltage range was: \(-1.05\) to \(+0.6\) V versus SCE. The electrolyte features were as follows: 0.1 M \(\text{NaOH}\) and 0.001 M \(\text{NaB}_1\text{H}_{12}\text{O}\).

Mass spectrometry experiments (MS; Waters Micromass, Wythenshawe, Manchester, UK; Quattro Micro mass spectrometer with electrospray ionization in negative mode) were performed to check the molecular weight of the anion \(\text{B}_1\text{H}_{12}\text{O}^-\) and to qualitatively analyze the oxidation by-products. Each sample (in solution) was analyzed by direct injection (FIA: flow injection analysis) using a Waters 2695 pump autosampler with a 20 \(\mu\)L loop. The mobile phase was a 50/50 (vol %) mixture of water and acetonitrile (both of HPLC grade). The spectrometer was operated at a constant flow rate such as 0.25 mL min\(^{-1}\). The detection conditions were as follows: capillary potential 3.5 kV; cone potential 30 V; source temperature 120 \degree \text{C}; desolvation temperature 450 \degree \text{C}; cone gas flow 50 L h\(^{-1}\); and desolvation gas flow 450 L h\(^{-1}\). The nebulizer gas was N\(_2\). The experimental spectrum of each identified chemical species (the identification being made on the basis of the available literature\(^2\)–\(^5\) and on assimilating the \(m/z\) value to a molecular weight) was then compared to the modeled spectrum (calculated from the supposed molecular weight) to confirm the identification made.

Impedance measurements were performed on a broadband dielectric spectrometer and Novocontrol alpha analyzer, over a frequency range from 0.01 Hz to 1 MHz with an applied ac voltage of 1 V. The temperature of the sample was controlled by the Quatro Novocontrol system. Measurements were collected from 150 to 0 \degree \text{C} on the anhydrous solid, obtained by in situ heating at 150 \degree \text{C} for 2 h. The measurements were performed on a pellet, with 0.5 and 12 mm of thickness and diameter, respectively, and using the two-probe method.

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**Notes**

The authors declare no competing financial interest.

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