



HAL
open science

Alkaline aqueous solution of sodium decahydro-closo-decaborate $\text{Na}_2\text{B}_{10}\text{H}_{10}$ as liquid anodic fuel

Salem Ould-Amara, Eddy Petit, Dominique Granier, Pascal Yot, Umit Demirci

► To cite this version:

Salem Ould-Amara, Eddy Petit, Dominique Granier, Pascal Yot, Umit Demirci. Alkaline aqueous solution of sodium decahydro-closo-decaborate $\text{Na}_2\text{B}_{10}\text{H}_{10}$ as liquid anodic fuel. *Renewable Energy*, 2019, 143, pp.551-557. 10.1016/j.renene.2019.05.019 . hal-02146573

HAL Id: hal-02146573

<https://hal.umontpellier.fr/hal-02146573v1>

Submitted on 22 Oct 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

1 Alkaline aqueous solution of sodium decahydro-*closo*- 2 decaborate $\text{Na}_2\text{B}_{10}\text{H}_{10}$ as liquid anodic fuel

3
4 Salem OULD-AMARA,¹ Eddy PETIT,² Dominique GRANIER,² Pascal G. YOT,² Umit B.
5 DEMIRCI^{1,*}

6 ¹ Institut Européen des Membranes, IEM – UMR 5635, ENSCM, CNRS, Univ Montpellier, Montpellier, France

7 ² Institut Charles Gerhardt Montpellier, ICGM – UMR 5253, CNRS, ENSCM, Univ Montpellier, Montpellier,
8 France

9 *Corr. author: umit.demirci@umontpellier.fr

10

11

12 Abstract

13 The potential of the decahydro-*closo*-decaborate anion $\text{B}_{10}\text{H}_{10}^{2-}$ in alkaline aqueous solution as
14 anodic fuel was investigated by using cyclic voltammetry and three different bulk metal
15 electrodes (platinum, gold and silver). The sodium salt $\text{NaB}_{10}\text{H}_{10}$ was first synthesized, fully
16 characterized and assessed for its relative stability in alkaline medium for 25 days. Then,
17 oxidation of $\text{B}_{10}\text{H}_{10}^{2-}$ in alkaline aqueous solution was studied. With platinum, the
18 electrochemical activity is nil. With gold and silver, oxidation takes place at >0 V vs. SCE,
19 suggesting direct oxidation of $\text{B}_{10}\text{H}_{10}^{2-}$. A current density of *e.g.* 15.1 mA cm^{-2} at 0.51 V vs. SCE
20 is produced, supporting an electrocatalytically activity for both electrodes. There is even some
21 reversibility of the process (*i.e.* reduction of intermediate species) with silver. The most important
22 oxidation products were identified as being B_7 -based anions for both silver and gold. Such results
23 suggest the occurrence of partial oxidative degradation of $\text{B}_{10}\text{H}_{10}^{2-}$ at positive potential and may
24 open new application prospects to polyborate anions.

25

26

27 Keywords

- 1 Anodic liquid fuel; Boron cluster; $\text{Na}_2\text{B}_{10}\text{H}_{10}$; Oxidation; Polyborate anion; Sodium decahydro-
- 2 *closo*-decaborate

1. Introduction

In the recent decades huge efforts have been dedicated to the development of a wide variety of materials for energy/hydrogen storage [1], including boron hydrides [2]. A typical and early example is sodium borohydride NaBH_4 , much investigated for hydrogen storage [3] and as anodic fuel for chemical energy storage [4]. A more recent example is sodium dodecahydro-*closo*-dodecaborate $\text{Na}_2\text{B}_{12}\text{H}_{12}$. It belongs to the family of the polynuclear borane anion-based salts [5], which have been considered: (i) for hydrogen storage and production (by hydrolysis) [6]; (ii) as anodic fuel for chemical energy storage [7]; and (iii) as solid electrolyte in electrochemical energy storage [8].

Both of the aforementioned boron hydrides have been considered as potential carbon-free anodic fuels owing to their solubility and relative stability in water. With respect to the borohydride anion BH_4^- , it spontaneously hydrolyzes when put into contact with water, which results in hydrogen evolution [9]:



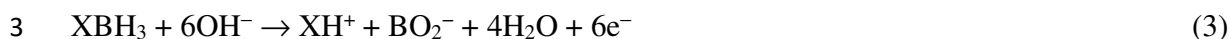
The reaction can be drastically limited by increasing the solution pH up to 10-13 [10]. The as-obtained alkaline aqueous solution of BH_4^- is then an attractive anodic fuel ($E^\circ = -1.24 \text{ V}$) [11]:



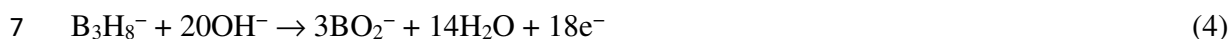
The resulting open circuit potential is as high as 1.64 V. A lot of efforts have been made to develop the related direct borohydride fuel cell technology but the progression objectives have been impeded by several critical issues [12]. One of the main problems relates to the unwanted hydrolysis reaction. It very slowly takes place even in alkaline conditions [10], but more critically it catalytically takes place over the metal electrode [13,14]. One of the main challenges ahead is to better understand the oxidation and hydrolysis mechanisms in order to search for novel anode electrocatalysts allowing depressed hydrogen evolution and making the electro-oxidation of BH_4^- an eight- or near-eight-electron process [15].

Alternatively, other boron hydrides, most being derivatives of NaBH_4 [2], have been considered. For example, oxidations of alkaline aqueous solutions of ammonia borane NH_3BH_3 , dimethylamine borane $(\text{CH}_3)_2\text{HNBH}_3$, hydrazine borane $\text{N}_2\text{H}_4\text{BH}_3$ and hydrazine *bis*borane

1 N₂H₄(BH₃)₂ over carbon-supported platinum and palladium nanoparticles were investigated and
2 the boranes were compared each other [16]:



4 where X is equal to NH₃, N₂H₄ and NH(CH₃)₂. For each of the boranes, oxidation is in
5 competition with heterogeneous hydrolysis, the H₂ evolution being more important over the
6 platinum electrode. Another potential boron hydride is the octahydrotriborate anion B₃H₈⁻ [17]:



8 It oxidizes over a bulk gold electrode but the effective number of electrons is about 10 out of a
9 theoretical total of 18 electrons (Eq. 4). Complete oxidation is not effective because
10 heterogeneous hydrolysis. A last potential boron hydride was recently proposed. Oxidation of the
11 dodecahydro-*closo*-dodecaborate anion B₁₂H₁₂⁻ was studied with platinum, gold and silver
12 electrodes [7]. The anion was chosen owing to its high stability in aqueous solution at any pH (no
13 hydrolysis). Partial oxidative degradation through a complex oxidation process was evidenced.
14 One of the products was identified as being B₁₁H₁₁O(OH)⁻ and its formation was tentatively
15 suggested to take place as follows:



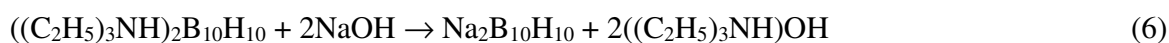
17 The most attractive feature with B₁₂H₁₂⁻ is the absence of heterogeneous hydrolysis. The
18 evolving electrons are all due to partial oxidation of the anion.

19
20 The recent achievements briefly described above created a window of opportunity for alkaline
21 aqueous solutions of polynuclear borane anions as possible anodic fuels. In the present work we
22 examined the potential of the decahydro-*closo*-decaborate anion B₁₀H₁₀²⁻ because, after the anion
23 B₁₂H₁₂²⁻, it is the second most stable species against hydrolysis [18]. The sodium salt, *i.e.*
24 Na₂B₁₀H₁₀, was synthesized and the successful synthesis and the purity of the sample were
25 verified. Its stability in aqueous solution was investigated so as to launch oxidation experiments.
26 Herein is reported, for the first time, the oxidation behavior of the anion B₁₀H₁₀²⁻ with platinum,
27 gold and silver bulk electrodes.

28
29
30

2. Material and Methods

Na₂B₁₀H₁₀ was prepared from the commercially available triethylammonium decahydro-*closo*-decaborate of formulae ((C₂H₅)₃NH)₂B₁₀H₁₀ (Katchem, 98%) by cationic substitution in alkaline medium:



The synthesis was performed under argon atmosphere. A 2-gram aliquot of ((C₂H₅)₃NH)₂B₁₀H₁₀ was dispersed in 100 mL of an alkaline aqueous (0.13 M NaOH) solution at room temperature. The suspension was heated at 90°C for 2 h, resulting in the formation of a clear solution. A white powder consisting of Na₂B₁₀H₁₀ was recovered by water extraction under vacuum.

The molecular structure of Na₂B₁₀H₁₀ was analyzed by Fourier-transform infrared spectroscopy (FTIR; Nicolet™ IS50 Thermo Fisher Scientific; 32 scans), nuclear magnetic resonance (NMR; Bruker AVANCE-300; ¹H such as probe head dual ¹H, 300.13 MHz, CD₃CN, and 30 °C; ¹¹B such as probe head BBO10, 79.39 MHz, D₂O, 30 °C). The crystal structure of Na₂B₁₀H₁₀ was analyzed by X-ray powder diffraction (XRPD) using a PANalytical X'Pert diffractometer equipped with an X'Celerator detector Si (111) monochromator. An operation voltage of 40 kV and an intensity of 40 mA were imposed to deliver the wavelength Cu-K_{α1}: λ = 1.54059 Å. The thermal stability of Na₂B₁₀H₁₀ was analyzed by thermogravimetric analysis (TGA; TA Instruments Q500; aluminum crucible of 40 μL, heating rate 5°C min⁻¹, under N₂ flow of 60 mL min⁻¹) as well as differential scanning calorimetric (DSC; TA Instruments 2920 MDSC; conditions identical to the TGA experiment).

The oxidation of the anion B₁₀H₁₀²⁻ (of Na₂B₁₀H₁₀ in aqueous solution) was studied by cyclic voltammetry (with a μAutolab® Type III potentiostat). A borosilicate cell of 100 mL was used (thermostated at 20°C). It was systematically, and before each experiment, cleaned with peroxymonosulfuric acid H₂SO₅ (Caro's Acid). Outgassed Milli-Q Water (18.2 MΩ cm, < 3 ppb total organic carbon) was used. The electrodes were as follows: saturated calomel electrode (SCE) as reference electrode; platinum wire as counter electrode; and a rotating disk (with bulk platinum Ø 2 mm, or bulk gold Ø 2 mm, or bulk silver Ø 4 mm) as working electrode. We selected platinum, gold and silver because, historically, they have been among the most

1 investigated metals for oxidation of the anion BH_4^- [12-15]; otherwise, we use to consider these
2 metals only, for screening any new B-based anodic fuel, since we well know about their catalytic
3 behavior towards the unwanted hydrolysis of BH_4^- . The surface of the working electrodes was
4 polished with diamond paste. The electrolyte solution was prepared from an aqueous solution of
5 NaOH at the concentration of 0.1 M. The concentration of $\text{B}_{10}\text{H}_{10}^{2-}$ was 0.001 M; it was kept so
6 low to limit the interactions between the molecules. The cell voltage range was fixed as follows:
7 -1.05 to $+0.6$ V vs. SCE (in order to avoid water splitting).
8

9 Mass spectrometry (MS) experiments allowed qualitative analyses of the oxidation by-products.
10 A Quattro Micro mass spectrometer, with electrospray ionization in negative mode (from Waters
11 Micromass; Wythenshawe, Manchester, UK) and operating at constant flow rate (0.25 mL min^{-1})
12 was used. The electrolyte samples taken were analyzed by direct injection (Waters 2695 pump-
13 autosampler, with $5 \mu\text{L}$ loop). A mixture of water and acetonitrile (50/50 in vol. %) was used as
14 mobile phase. The nebulizer gas was N_2 . For detection, the conditions were: capillary potential of
15 3.5 kV ; cone potential of 30 V ; source temperature at 120°C ; desolvation temperature at 450°C ;
16 cone gas flow of 50 L h^{-1} ; desolvation gas flow of 450 L h^{-1} . The recorded m/z values were
17 compared to comparable molecular weights (of polyborate anions) and then the experimental
18 spectra were compared to modeled/calculated spectra in order to confirm the identifications
19 made.
20
21

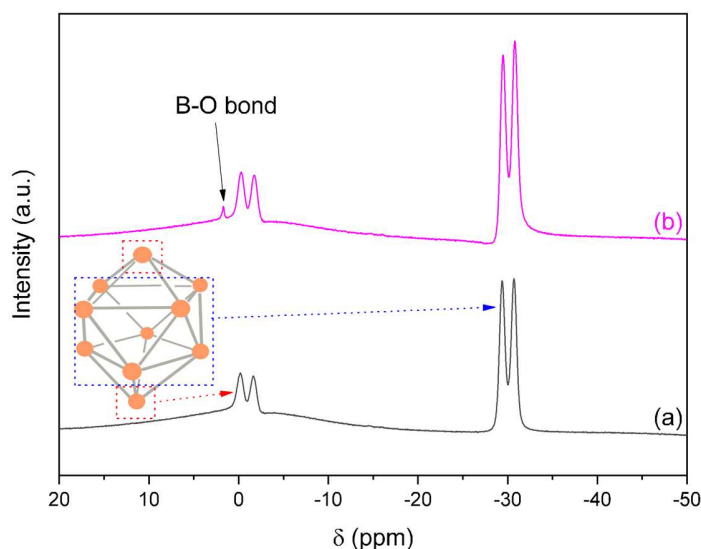
22 3. Results and discussion

23 3.1. Characterizations of $\text{Na}_2\text{B}_{10}\text{H}_{10}$

24 The ^{11}B NMR spectrum of the anion $\text{B}_{10}\text{H}_{10}^{2-}$ (Figure 1) shows two doublets centered at -1 ppm
25 ($J_{\text{BH}} = 140.1 \text{ Hz}$) and -29 ppm ($J_{\text{BH}} = 125.4 \text{ Hz}$), suggesting two kinds of boron environments in
26 the molecule (2 equivalent apical boron atoms + 8 equivalent equatorial boron atoms) [19]. The
27 relative area of these doublets is 4 to 1, which is in good agreement with the equatorial 8 boron
28 atoms and the 2 apex boron atoms [20,21]. The purity of the sample is also confirmed.
29

1 The ^1H NMR spectrum of the anion $\text{B}_{10}\text{H}_{10}^{2-}$ (**Figure 2**) is characterized by several signals, apart
2 from those due to the solvent H_2O and to CH_3CN present in the deuterated solvent. There are two
3 sets of 7 peaks located between 4 and 2 ppm and between 1 and -1 ppm. They are typical of
4 $^{11}\text{B}-\text{H}$ and $^{10}\text{B}-\text{H}$ bonds [22,23], and are in good agreement with the presence of two B–H
5 environments in the molecular anion [24]. The relative area of these signals is 4 to 1, in good
6 agreement with the number of hydrogen elements bound to the equatorial 8 boron atoms and to
7 the 2 apex boron atoms.

8



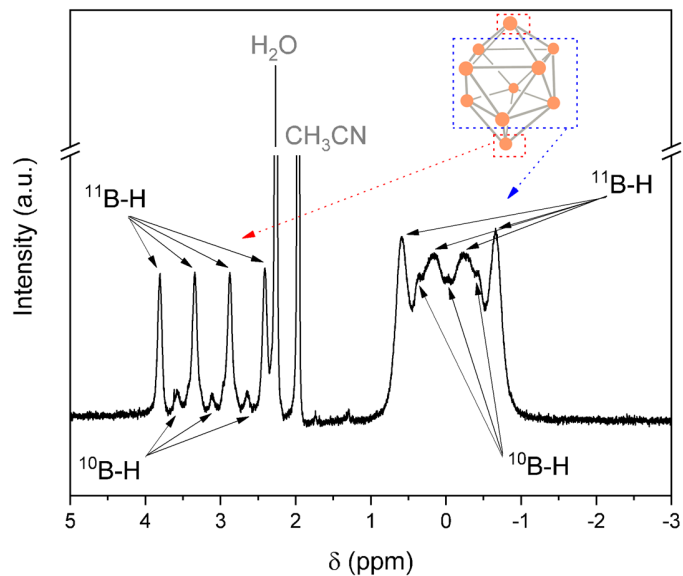
9

10 **Figure 1.** (a) ^{11}B NMR spectrum of the anion $\text{B}_{10}\text{H}_{10}^{2-}$ (from $\text{Na}_2\text{B}_{10}\text{H}_{10}$). (b) ^{11}B NMR spectrum of the anion $\text{B}_{10}\text{H}_{10}^{2-}$ in an alkaline
11 solution (1 M NaOH) after 25 days.

12

13 Analysis by FTIR spectroscopy was lastly performed on $\text{Na}_2\text{B}_{10}\text{H}_{10}$ (**Figure 3**). The vibration
14 bands at 2432 and 2461 cm^{-1} are favorably ascribed to stretching of the apical and equatorial
15 B–H bonds respectively. The bands between 1300 and 1050 cm^{-1} are due to the B–H bonds
16 deformation. The B–B bonds are featured by the band peaking at 1026 cm^{-1} . This is in good
17 agreement with the fingerprint of the molecular structure of $\text{B}_{10}\text{H}_{10}^{2-}$ [21,24]. There are
18 additional bands at $3600-3500$ and 1604 cm^{-1} that are ascribed to O–H bonds. The presence of
19 B–O–H environments (like in borates) is discarded by the NMR results presented above. These
20 signals may be ascribed to residual and/or adsorbing water molecules.

1



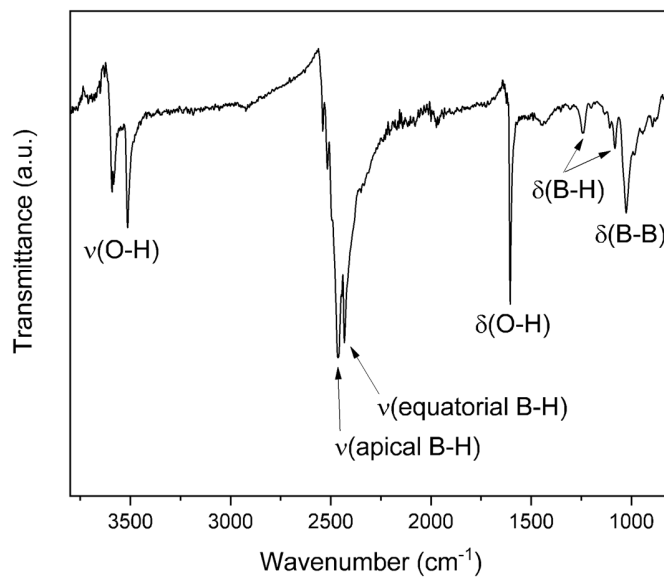
2

3

Figure 2. ^{11}H NMR spectrum of the anion $\text{B}_{10}\text{H}_{10}^{2-}$ (from $\text{Na}_2\text{B}_{10}\text{H}_{10}$).

4

5



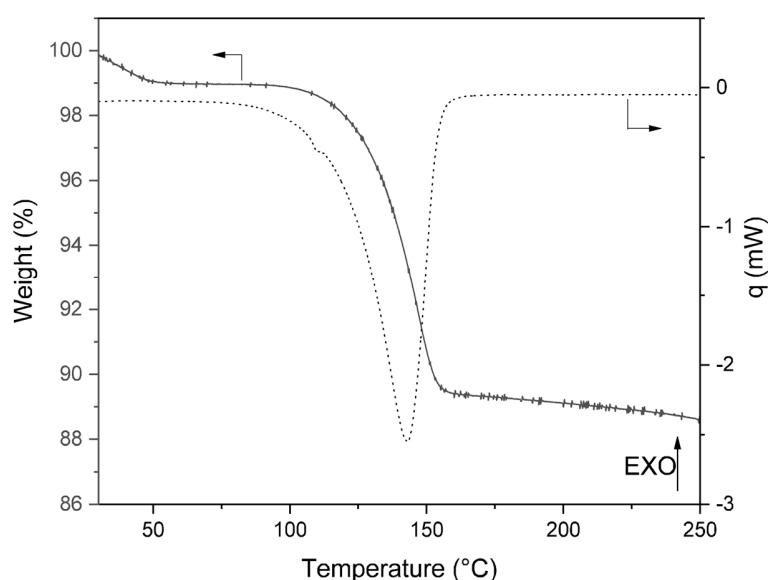
6

7

Figure 3. FTIR spectrum of $\text{Na}_2\text{B}_{10}\text{H}_{10}$.

1
2
3
4
5
6
7
8
9

Based on the FTIR observations, the thermally stable $\text{Na}_2\text{B}_{10}\text{H}_{10}$ was analyzed by TGA and DSC (Figure 4). Under heating, the sample suffers a first weight loss (1 wt%) up to 50°C and a second one, more important (9.6 wt%), between 100 and 160°C . The latter is featured by an endothermic process. The weight losses are much likely due to removal of adsorbed water as reported elsewhere [25]. The overall weight loss was considered to calculate the number of adsorbed water molecule per mole of $\text{Na}_2\text{B}_{10}\text{H}_{10}$. It was found about to be 1, suggesting the empirical formulae $\text{Na}_2\text{B}_{10}\text{H}_{10}\cdot\text{H}_2\text{O}$.

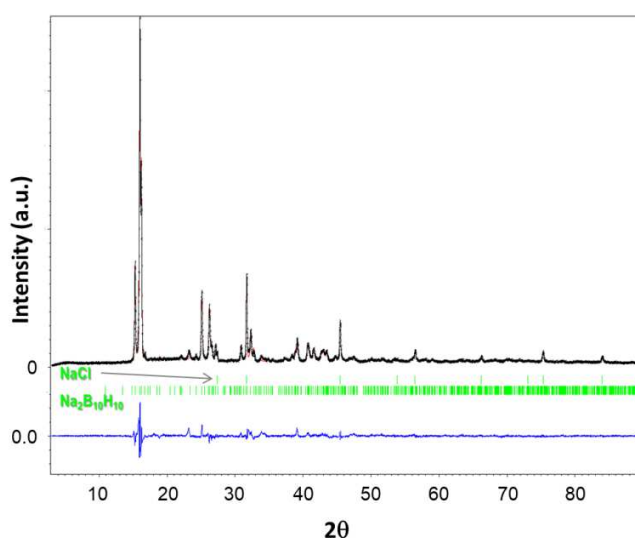


10
11
12

Figure 4. TGA and DSC results for $\text{Na}_2\text{B}_{10}\text{H}_{10}$.

13 $\text{Na}_2\text{B}_{10}\text{H}_{10}\cdot\text{H}_2\text{O}$ is a white solid. Following the results obtained by TGA and DSC, the powder
14 was placed into a 1 mm diameter glass capillary into a glove box then heat-treated at 110°C
15 overnight under primary vacuum (to remove the residual water molecules) and then sealed to
16 protect the as-obtained anhydrous $\text{Na}_2\text{B}_{10}\text{H}_{10}$ from hydration. The XRPD pattern of the sample
17 was finally recorded in the 2θ range 5° - 100° using the Debye-Scherrer method (Figure 5). The
18 solid is polycrystalline and the pattern is comparable to previously reported results [26,27]. In our
19 case, an impurity supposed to be NaCl ($a = 5.639(1) \text{ \AA}$, s.g. $Fm-3m$ (No. 225)) was fitted using

1 Le Bail method. **Figure 5** also presents the refinement of the pattern obtained using JANA2006
2 software [28]. The crystal structure was successfully solved in the monoclinic phase ($Z = 4$),
3 using the space group $P2_1/c$ (*No. 14*). The cell parameters were determined as: $a = 6.7228(6) \text{ \AA}$; b
4 $= 13.1435(11) \text{ \AA}$; $c = 11.9520(9) \text{ \AA}$; $\beta = 120.616(5)^\circ$; $V = 908.88(13) \text{ \AA}^3$ (GoF = 2.08; $R_p = 8.62$;
5 $wR_p = 11.47$; $R(\text{obs})/R(\text{all})$: 10.06/11.11; $wR(\text{obs})/wR(\text{all})$: 7.66/7.79). The result obtained for
6 the anhydrous phase $\text{Na}_2\text{B}_{10}\text{H}_{10}$ is in good agreement with the work previously reported in ref.
7 [26].
8



9
10 **Figure 5.** Result of the refinement carried out on the XRPD pattern of anhydrous $\text{Na}_2\text{B}_{10}\text{H}_{10}$ ($\lambda = 1.54059 \text{ \AA}$). The observed (in
11 black) and calculated (in red) XRPD profiles for the Rietveld refinement of $\text{Na}_2\text{B}_{10}\text{H}_{10}$ and Le Bail refinement of NaCl are shown.
12 The bottom curve (in blue) is the difference plot on the same scale intensity. The tic marks (in green) are the calculated angles
13 for the Bragg peaks for the two phases in 2θ .

14
15 To sum up, $\text{Na}_2\text{B}_{10}\text{H}_{10} \cdot \text{H}_2\text{O}$ was successfully prepared in our conditions. The sample is
16 monohydrated and contains a small amount of NaCl. This is not problematic for an anodic fuel
17 that has to be dissolved in alkaline aqueous solution. The presence of NaCl had nevertheless to be
18 kept in mind for the preparation of the 0.001 M $\text{Na}_2\text{B}_{10}\text{H}_{10} \cdot \text{H}_2\text{O}$ solution used as electrolyte.
19

20 3.2. Stability of $\text{B}_{10}\text{H}_{10}^{2-}$ in alkaline solution

21 As a preliminary step, the stability of $\text{B}_{10}\text{H}_{10}^{2-}$ (10^{-5} M) in alkaline solution (0.1 M NaOH) was
22 assessed. The fresh solution was analyzed by ^{11}B NMR and then was stored for 25 days before

1 being analyzed once more by ^{11}B NMR (**Figure 1**). A singlet of small intensity appeared at
2 positive chemical shifts (1.7 ppm). It is due to the formation of B–O bonds (by oxidation and/or
3 hydrolysis) like for borates. Despite this, it may be stated that the spectrum indicates a relatively
4 good stability of the anion in the aforementioned conditions. Alkaline solution of $\text{B}_{10}\text{H}_{10}^{2-}$ is
5 stable enough to be studied as possible anodic fuel.

6

7 3.3. Oxidation of $\text{B}_{10}\text{H}_{10}^{2-}$ over platinum

8 To our knowledge, oxidation of $\text{B}_{10}\text{H}_{10}^{2-}$ in alkaline conditions over a metal electrode has not
9 been investigated so far. An example of report available in the open literature deals with chemical
10 oxidation in acidic conditions resulting in the formation of B_{20} -based polynuclear borane anions
11 [29]. Another example is about oxidation by MnO_4^- at pH 7 and at room temperature, resulting in
12 quantitative conversion to boric acid $\text{B}(\text{OH})_3$ [30]. Accordingly, the electro-oxidation results
13 reported hereafter were analyzed with the help of the knowledge developed with the anion BH_4^-
14 [12-15,31] and in a lesser extent with the new boron hydride candidates [7,16,17].

15

16 The electro-oxidation of $\text{B}_{10}\text{H}_{10}^{2-}$ was first investigated with the platinum electrode (**Figure 6**) at
17 natural diffusion conditions (0 rpm). The voltammogram does not show apparent oxidation
18 and/or reduction processes. Additional experiments were performed with different rotation rates
19 (up to 2500 rpm) but no marked improvement was observed (voltammograms not reported). Such
20 results do not support bulk platinum as suitable electrode for electro-oxidation of $\text{B}_{10}\text{H}_{10}^{2-}$. In
21 comparison, the more-stable anion $\text{B}_{12}\text{H}_{12}^{2-}$ was found to oxidize over the same electrode at <0 V
22 vs. SCE, suggesting $\text{B}_{12}\text{H}_{12}^{2-}$ dissociative adsorption and oxidation of H_{ads} , together with some
23 direct partial oxidation of the anion [7]. The lack of apparent oxidation of $\text{B}_{10}\text{H}_{10}^{2-}$ could be
24 explained by an absence of adsorption of the anion onto the electrode surface.

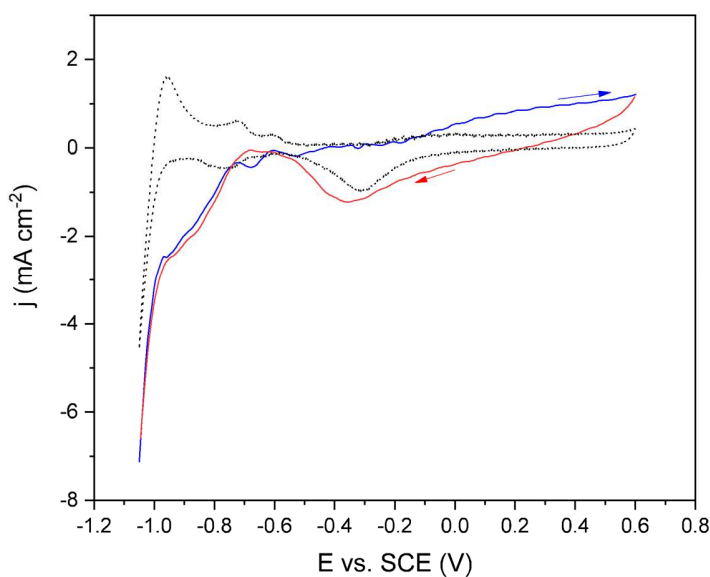
25

26 3.4. Oxidation of $\text{B}_{10}\text{H}_{10}^{2-}$ over gold

27 Gold has been much investigated as effective electrode for oxidation of a boron hydride like
28 NaBH_4 [12,15,31]. A bulk gold electrode was also considered in the present work (**Figure 7**).
29 Gold is unable to generate a current below -0.2 V vs. SCE. This suggests that it is neither able to
30 partially dissociate $\text{B}_{10}\text{H}_{10}^{2-}$ [14] nor to valorize adsorbed H species (H_{ads}) [7]. The only

1 oxidation peak (a_{Au}) appearing during the forward sweep is in the metal-(hydr)oxide region [13],
 2 namely at +0.24 V vs. SCE for a current density of 3.5 mA cm^{-2} . It may be due to direct (at least
 3 partial) oxidation of adsorbed $B_{10}H_{10}^{2-}$ [32]. A similar result was obtained with $B_{12}H_{12}^{2-}$ in
 4 similar conditions [7]. For both anions, the process is not reversible. In contrast, in the present
 5 work, there is an oxidation peak during the backward sweep: c_{Au} at 0 V vs. SCE (0.7 mA cm^{-2}). It
 6 is reasonable to suggest oxidation of intermediates (as well as that of $B_{10}H_{10}^{2-}$) [33] and/or
 7 oxidation of adsorbed H atoms [34]. Additional experiments were performed at disk rotation rates
 8 of 1000 and 2000 rpm (Figure 7). The current density for a_{Au} increases up to 4 mA cm^{-2} at 2000
 9 rpm (0.29 V vs. SCE). This is an indication of the low impact of poisoning, if it takes place, over
 10 the gold electrode [13].

11



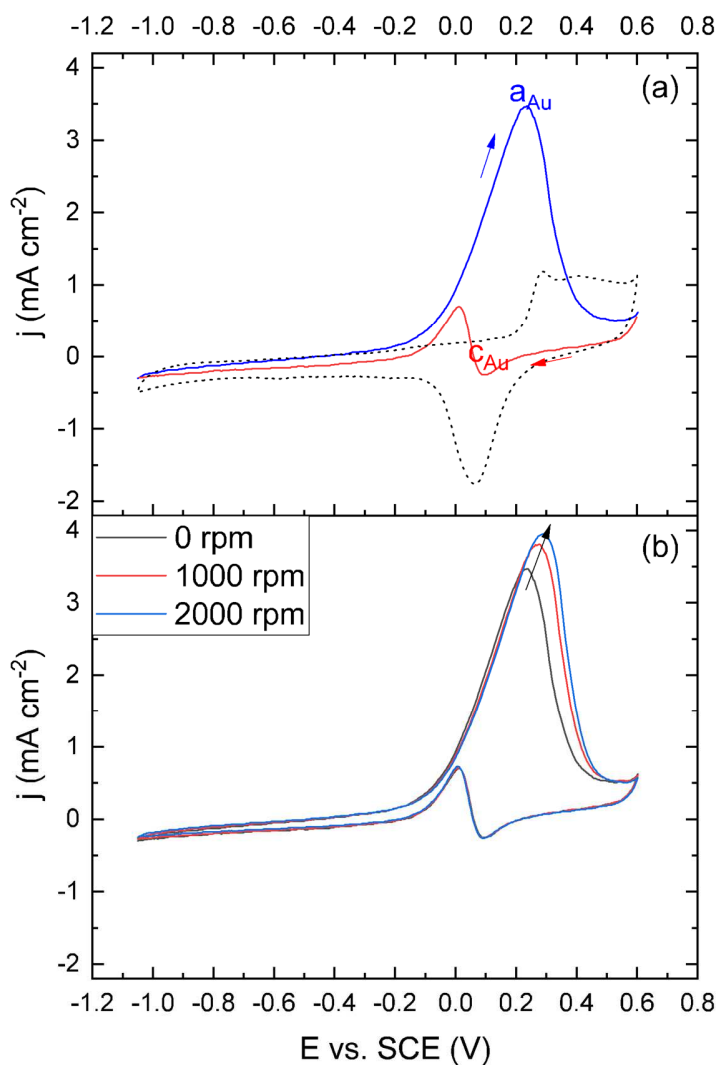
12

13 **Figure 6.** Cyclic voltammogram obtained on bulk platinum at 100 mV s^{-1} and at natural diffusion conditions (0 rpm). The
 14 voltammogram of 0.1 M NaOH (dashed lines) is superimposed to that of 0.1 M NaOH + 0.001 M $Na_2B_{10}H_{10}$ (solid lines). The blue
 15 line indicates the forward scan and the red line the backward scan, which are besides shown by two arrows.

16

17 Because of too low concentrations, the oxidation products could not be identified by ^{11}B NMR
 18 [7]. Instead, they were detected and qualitatively analyzed by MS. The CV experiment was
 19 repeated while respecting the following procedure: the potential was scanned from -1.05 to $+0.6$

1 V vs. SCE; there was no negative scan; 1000 successive scans were applied; and, every 100
2



3
4 **Figure 7.** (a) Cyclic voltammogram obtained on bulk gold at 100 mV s⁻¹ and at natural diffusion conditions (0 rpm). The
5 voltammogram of 0.1 M NaOH (dashed lines) is superimposed to that of 0.1 M NaOH + 0.001 M Na₂B₁₀H₁₀ (solid lines). The blue
6 line indicates the forward scan and the red line the backward scan, which are besides shown by two arrows. (b) Cyclic
7 voltammogram obtained on bulk platinum at 100 mV s⁻¹ and at different rotation rates of the disk electrode.

8
9 cycles an aliquot of the electrolyte was withdrawn to be analyzed by MS. Several m/z values were
10 detected ($m/z = 69, 99.3, 100.4, 102.3, 116.7$), suggesting products formed by partial oxidative
11 degradation of B₁₀H₁₀²⁻ (118 g mol⁻¹). One of them ($m/z = 99.3$) was found to be predominant
12 and it may be ascribed to B₇H₈O⁻. It is followed by the m/z value of 102.3, possibly due to

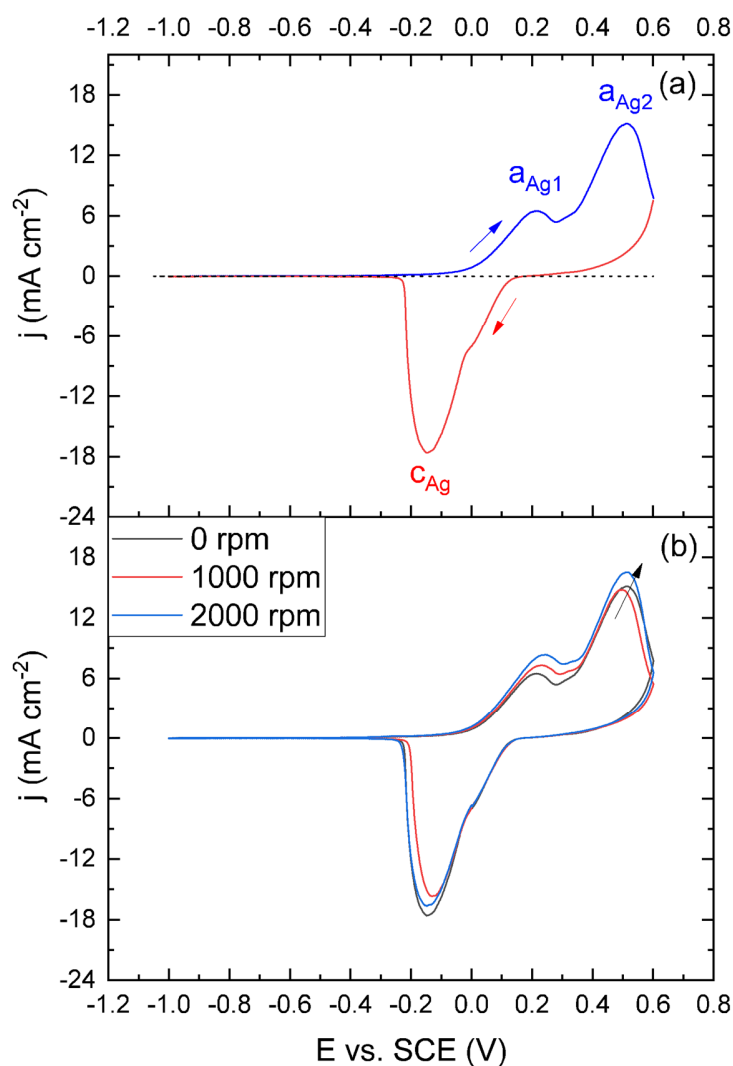
1 B₇H₁₁O⁻. The others were in fact detected in much lesser amounts and their identification has
2 been difficult: the *m/z* values of 100.4 and 116.7 suggest species containing 7 boron atoms (*e.g.*
3 B₇H₉O⁻ and B₇H₉O₂⁻); and the *m/z* values of 69 might be ascribed to a species with 4 boron
4 atoms (*e.g.* B₄H₁₀O⁻). Though the identification of all of the species is difficult, the MS results
5 are thus in good agreement with the CV results implying partial oxidation of B₁₀H₁₀²⁻.

6

7 3.5. Oxidation of B₁₀H₁₀²⁻ over silver

8 Bulk silver was also considered as possible working electrode (**Figure 8**). The forward step is
9 featured by two oxidation peaks: a_{Ag1} at 0.22 V vs. SCE with 6.5 mA cm⁻², and a_{Ag2} at 0.51 V vs.
10 SCE with 15.1 mA cm⁻². The first peak is comparable to that observed with the gold electrode
11 and may be attributed to direct (at least partial) oxidation of B₁₀H₁₀²⁻ [32]. With respect to the
12 second oxidation wave, it may be also attributed to direct and possibly more complete oxidation
13 of B₁₀H₁₀²⁻ [35] as well as to oxidation of adsorbed reaction intermediates [33]. The electro-
14 oxidation ability of bulk silver is slightly better than that of bulk gold, making silver a more
15 attractive candidate for further works on electrode materials. With BH₄⁻, silver oxide was
16 reported to be the electroactive surface responsible of the direct oxidation of the adsorbed
17 intermediate BH₃OH⁻ at similar potentials [36]. Surface species such as Ag(O_xH_yB_z) were
18 reported elsewhere [7]. The backward step of the voltammogram shows a reduction (c_{Ag} at -0.15
19 V vs. SCE with -17.6 mA cm⁻²) of, much likely, an oxidation product. Such a reduction wave let
20 us suggest that the electrochemical process involving B₁₀H₁₀²⁻ and silver is, at least partly,
21 reversible: one (or more) of the species (see below for identified products) forming during the
22 oxidation waves a_{Ag1} and a_{Ag2} is reduced at -0.15 V vs. SCE (wave c_{Ag}). The effect of the rotation
23 rate of the disk electrode does not have a negative effect on the current density, which slightly
24 increases along with the higher speed of the rate. Like for the gold electrode, this is an indication
25 of the low impact of poisoning on the surface of bulk silver [13]. Comparable results were
26 obtained with B₁₂H₁₂²⁻ in identical operation conditions but the current densities were 4 times
27 higher (at about 0.5 V vs. SCE) [7].

28



1
 2 **Figure 8.** (a) Cyclic voltammogram obtained on bulk silver at 100 mV s^{-1} and at natural diffusion conditions (0 rpm). The
 3 voltammogram of 0.1 M NaOH (dashed lines) is superimposed to that of 0.1 M NaOH + 0.001 M $\text{Na}_2\text{B}_{10}\text{H}_{10}$ (solid lines). The blue
 4 line indicates the forward scan and the red line the backward scan, which are besides shown by two arrows. (b) Cyclic
 5 voltammogram obtained on bulk platinum at 100 mV s^{-1} and at different rotation rates of the disk electrode.

6
 7 Considering the above-reported cyclic voltammetry performances, the bulk electrodes can be
 8 discussed in terms of electrochemical activity. In our conditions, the highest current density was
 9 measured for bulk silver (followed by gold), making it the best candidate. Platinum is
 10 electrocatalytically inactive. Over silver and gold, the oxidation processes require high potentials
 11 (e.g. 0.51 V vs. SCE for $a_{\text{Ag}2}$ in **Figure 8**) and take place in the metal-oxide region, showing thus
 12 the importance of surface (hydr)oxides in oxidation of $\text{B}_{10}\text{H}_{10}^{2-}$. Though the present results are

1 mixed, there are interesting and open opportunities for improvement. The potential of alkaline
2 aqueous $B_{10}H_{10}^{2-}$ as anodic fuel would depend on the development of multimetallic electrodes in
3 order to achieve lower oxidation potentials (more realistic for a fuel cell application) and higher
4 current densities (*via* complete oxidation). With the much-investigated BH_4^- , such improvements
5 were reported for *e.g.* Au-Cu [37,38], Ag-Cu [39] and Ag-Pt alloys [40].

6
7 The oxidation products forming over bulk silver were analyzed by MS by repeating the CV
8 experiment and following the conditions described for the gold electrode. Several m/z signals
9 were detected. Only one signal ($m/z = 102.3$, ascribed to $B_7H_{11}O^-$) predominated. This species
10 could be that reducing during the backward step of the CV experiment (Figure 8). The other m/z
11 signals could be considered as minor ($m/z = 145$, suggested to belong to *e.g.* $B_{11}H_{10}O^-$) or very
12 minor products ($m/z = 100.4$ possibly for $B_7H_9O^-$, 116.7 probably due to $B_7H_9O_2^-$, and 142.6 for
13 an unidentified compound). These results clearly indicate the partial oxidative degradation of
14 $B_{10}H_{10}^{2-}$ over the silver electrode and support the CV results discussed above.

17 4. Conclusion

18 The potential of the decahydro-*closo*-decaborate anion $B_{10}H_{10}^{2-}$ (in alkaline aqueous solution) as
19 anodic fuel (ultimately for direct liquid-fed fuel cell) was considered and assessed with the help
20 of cyclic voltammetry and by using three different bulk metal electrodes such as platinum, gold
21 and silver. As a first step the sodium salt was synthesized and the obtained white solid was
22 characterized and identified by NMR, FTIR and XRPD. Rather stable in alkaline medium
23 (oxidation in small extent with formation of B–O bonds after 25 days in a solution at 0.1 M
24 NaOH), the anion $B_{10}H_{10}^{2-}$ was found to be suitable for the cyclic voltammetry experiments.
25 With the bulk platinum electrode, the electrochemical activity is nil. In contrast, with bulk gold
26 and silver, oxidation takes place at potentials higher than 0 V *vs.* SCE, suggesting direct
27 oxidation of $B_{10}H_{10}^{2-}$. There is some reversibility of the oxidation process with the silver
28 electrode. Both electrodes are electrocatalytically active and allow the production of current
29 densities (*e.g.* 15.1 mA cm^{-2} at 0.51 V vs. SCE) that are however low for the targeted ultimate
30 application. The most important oxidation products were identified by MS. The anion $B_7H_8O^-$

1 predominates for the gold electrode while $B_7H_{11}O^-$ is the preponderate species for bulk silver. In
2 both cases, the results suggest the occurrence of partial oxidative degradation of $B_{10}H_{10}^{2-}$ at
3 positive potentials. From the present work there are thus three conclusions to be drawn. First, the
4 well-known stability of the polynuclear borane anions is, to a certain extent, confirmed. In our
5 conditions, $B_{10}H_{10}^{2-}$ is stable towards oxidation over bulk platinum and it slightly oxidizes over
6 gold and silver. Second, partial oxidative degradation of $B_{10}H_{10}^{2-}$ over the last two electrodes
7 could be valorized differently, namely by focusing on the synthesis of species like $B_7H_8O^-$ and
8 $B_7H_{11}O^-$ provided novel and advanced electrodes are developed for improved conversion and
9 selectivity. Third, silver appears to be the best metal when alkaline aqueous $B_{10}H_{10}^{2-}$ is considered
10 as potential anodic fuel. However, the oxidation potentials are high and the current densities
11 relatively low (in comparison to *e.g.* performance of the much-investigated BH_4^-).
12 Notwithstanding, the anion $B_{10}H_{10}^{2-}$ should not be discarded from the targeted application
13 because of very attractive theoretical properties (*cf.* supplementary information): (i) a total
14 oxidation of $B_{10}H_{10}^{2-}$ could generate up to 22 electrons; (ii) the theoretical oxidation potential is
15 as low as -3.3 V; and (iii) the theoretical specific energy of a fuel cell based on the couple
16 $B_{10}H_{10}^{2-}/O_2$ would be as high as *ca.* 18500 Wh kg^{-1} , which is much higher than the theoretical
17 specific energy of a number of liquid fuels [41]. However further works are necessary to make
18 $B_{10}H_{10}^{2-}$ useable and this calls for developments of silver-based multimetallic electrodes
19 efficiently operating at low potential.

20

21

22 Acknowledgements

23 This work was supported by the ANR Agence Nationale de la Recherche [program
24 “Investissements d’Avenir”, LabEx CheMISyst, grant number ANR-10-LABX-05-01]; the
25 Région Languedoc-Roussillon [program “Chercheur(se)s d’Avenir 2013”, project C3, grant
26 number 2013 008555]. We thank Prof. M. Cretin (IEM, Univ Montpellier) for accessibility to
27 cyclic voltammetry.

28

29

1 References

- 2 [1] C. Liu, F. Li, H.M. Cheng, Advanced materials for energy storage, *Adv. Mater.* 22 (2011)
3 E28–E62.
- 4 [2] U.B. Demirci, Sodium borohydride for the near-future energy: a “rough diamond” for
5 Turkey, *Turk. J. Chem.* 42 (2018) 193–220.
- 6 [3] P. Brack, S.E. Dann, K.G.U. Wijayantha, Heterogeneous and homogenous catalysts for
7 hydrogen generation by hydrolysis of aqueous sodium borohydride (NaBH_4) solutions,
8 *Energy Env. Eng.* 3 (2015) 174–188.
- 9 [4] M.C. Sison Escaño, R.L. Arevalo, E. Gyenge, H. Kasai, Electrocatalysis of borohydride
10 oxidation: a review of density functional theory approach combined with experimental
11 validation, *J. Phys.: Condens. Matter* 26 (2014) 353001:1–14.
- 12 [5] R.E. Williams, The polyborane, carborane, carbocation continuum: architectural patterns,
13 *Chem. Rev.* 92 (1992) 177–207.
- 14 [6] A.V. Safronov, S.S. Jalisatgi, H.B. Lee, M.F. Hawthorne, Chemical hydrogen storage
15 using polynuclear borane anion salts, *Int. J. Hydrogen Energy* 36 (2011) 234–239.
- 16 [7] S. Pylypko, S. Ould-Amara, A. Zadick, E. Petit, M. Chatenet, M. Cretin, U.B. Demirci,
17 The highly stable aqueous solution of sodium dodecahydro-*closo*-dodecaborate
18 $\text{Na}_2\text{B}_{12}\text{H}_{12}$ as a potential liquid anodic fuel, *Appl. Catal. B Env.* 222 (2018) 1–8.
- 19 [8] N. Verdala, J.H. Her, V. Stavila, A.V. Soloninin, O.A. Babanova, A.V. Skripov, T.J.
20 Udovic, J.J. Rush, Complex high-temperature phase transitions in $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and
21 $\text{Na}_2\text{B}_{12}\text{H}_{12}$, *J. Sol. State Chem.* 212 (2014) 81–91.
- 22 [9] M.V. Mirkin, H. Yang, A.J. Bard, Borohydride oxidation at a gold electrode, *J.*
23 *Electrochem. Soc.* 139 (1992) 2212–2217.
- 24 [10] M.M. Kreevoy, J.E.C. Hutchins, H_2BH_3 as an intermediate in tetrahydridoborate
25 hydrolysis, *J. Am. Chem. Soc.* 94 (1972) 6371–6376.
- 26 [11] M.E. Indig, R.N. Snyder, Sodium borohydride, an interesting anodic fuel, *J. Electrochem.*
27 *Soc.* 109 (1962) 1104–1106.
- 28 [12] J. Ma, Y. Sahai, Direct borohydride fuel cells – Current status, issues, and future
29 directions, in: L. An, T.S. Zhao (Eds.), *Anion exchange membrane fuel cells*, Springer
30 International Publishing AG, Cham, 2018, pp. 249–273.

- 1 [13] G. Braesch, A. Bonnefont, V. Martin, E.R. Savinova, M. Chatenet, Borohydride oxidation
2 reaction mechanisms and poisoning effects on Au, Pt and Pd bulk electrodes: From model
3 (low) to direct borohydride fuel cell operating (high) concentrations, *Electrochim. Acta*
4 273 (2018) 483-494.
- 5 [14] P.Y. Olu, A. Bonnefont, G. Braesch, V. Martina, E.R. Savinova, M. Chatenet, Influence
6 of the concentration of borohydride towards hydrogen production and escape for
7 borohydride oxidation reaction on Pt and Au electrodes – experimental and modelling
8 insights, *J. Power Sources* 375 (2018) 300–309.
- 9 [15] J.M. Nurul, A. Choudhury, Y. Sahai, A comprehensive review of direct borohydride fuel
10 cells, *Renew. Sust. Energy Rev.* 14 (2010) 183–199.
- 11 [16] A. Zadick, J.F. Petit, V. Martin, L. Dubau, U.B. Demirci, C. Geantet, M. Chatenet,
12 Ubiquitous borane fuel electrooxidation on Pd/C and Pt/C electrocatalysts: toward
13 promising direct hydrazine-borane fuel cells, *ACS Catal.* 8 (2018) 3150–3163.
- 14 [17] S. Pylypko, A. Zadick, M. Chatenet, P. Miele, M. Cretin, U.B. Demirci, A preliminary
15 study of sodium octahydrotriborate NaB_3H_8 as potential anodic fuel of direct liquid fuel
16 cell, *J. Power Sources* 286 (2015) 10–17.
- 17 [18] F. Klanberg, E.L. Muetterties, Chemistry of boranes. XXVII. New polyhedral borane
18 anions, $\text{B}_9\text{H}_9^{2-}$ and $\text{B}_{11}\text{H}_{11}^{2-}$, *Inorg. Chem.* 5 (1966) 1955–1960.
- 19 [19] D. Gabel, S. Mai, O. Perleberg, The formation of boron–carbon bonds to closo-
20 decaborate(2–) and closo-dodecaborate(2–)), *J. Organomet. Chem.* 581 (1999) 45–50.
- 21 [20] W.I. Lipscomb, A.R. Pitochelli, M.F. Hawthorne, Probable structure of the $\text{B}_{10}\text{H}_{10}^{2-}$
22 anion, *J. Am. Chem. Soc.* 81 (1959) 5833–5834.
- 23 [21] E.L. Muetterties, J.H. Balthis, Y.T. Chia, W.H. Knoth, H.C. Miller, Chemistry of boranes.
24 VIII. Salts and acids of $\text{B}_{10}\text{H}_{10}^{2-}$ and $\text{B}_{12}\text{H}_{12}^{2-}$, *Inorg. Chem.* 3 (1964) 444–451.
- 25 [22] D. Reed, The role of NMR in boron chemistry, *Chem. Soc. Rev.* 22 (1993) 109–116.
- 26 [23] T. Ruman, A. Kuśnierz, A. Jurkiewicz, A. Leś, W. Rode, The synthesis, reactivity and ^1H
27 NMR investigation of the hydroxyborohydride anion, *Inorg. Chem. Commun.* 10 (2007)
28 1074–1078.
- 29 [24] E.S. Shubina, E.V. Bakhmutova, A.M. Filin, I.B. Sivaev, L.N. Teplitskaya, A.L.
30 Chistyakov, I.V. Stankevich, V.I. Bakhmutov, V.I. Bregadze, L.M. Epstein, Dihydrogen
31 bonding of decahydro-closo-decaborate(2–) and dodecahydro-closo-dodecaborate(2–)

- 1 anions with proton donors: experimental and theoretical investigation, *J. Organomet.*
2 *Chem.* 657 (2002) 155–162.
- 3 [25] V.K. Skachkova, L.V. Goeva, A.V. Grachev, V.V. Avdeeva, E.A. Malinina, A.Yu.
4 Shaulov, A.A. Berlin, N.T. Kuznetsov, Thermal and thermo-oxidative properties of the
5 decahydro-closo-decaborate anion $B_{10}H_{10}^{2-}$ in a silicate matrix, *Inorg. Mater.* 51 (2015)
6 736–740.
- 7 [26] K. Hofmann, B. Albert, Crystal structures of $M_2[B_{10}H_{10}]$ ($M = Na; K; Rb$) via real-space
8 simulated annealing powder techniques, *Z. Kristallogr.* 220 (2005) 143–146.
- 9 [27] H. Wu, W.S. Tang, W. Zhou, V. Stavila, J.J. Rush, T.J. Udovic, The structure of
10 monoclinic $Na_2B_{10}H_{10}$: a combined diffraction, spectroscopy, and theoretical approach,
11 *Cryst. Eng. Commun.* 17 (2015) 3533–3540.
- 12 [28] V. Petricek, M. Dusek, L. Palatinus, Crystallographic computing system JANA2006:
13 general features, *Z. Kristallogr.* 3 (2014) 345–352.
- 14 [29] B.L. Chamberland, E.L. Muetterties, Chemistry of boranes. XVIII. Oxidation of $B_{10}H_{10}^{2-}$
15 and its derivatives, *Inorg. Chem.* 3 (1964) 1450–1456.
- 16 [30] A. Kaczmarczyk, G.B. Koiski, W.P. Townsend, Oxidative degradation of polyhedral
17 boranes, *J. Am. Chem. Soc.* 87 (1965) 1413–1413.
- 18 [31] P. Rodriguez, M.T.M. Koper, Electrocatalysis on gold, *Phys. Chem. Chem. Phys.* 16
19 (2014) 13583–13594
- 20 [32] M. Chatenet, M.B. Molina-Concha, J.P. Diard, First insights into the borohydride
21 oxidation reaction mechanism on gold by electrochemical impedance spectroscopy,
22 *Electrochim. Acta* 54 (2009) 1687–1693.
- 23 [33] D.R. Smith, E.B. Rupp, D.F. Shriver, The mechanisms of electrolytic reduction for
24 decaborane(14), $B_{10}H_{14}$, in an aprotic solvent. II. The second reduction step and the
25 reduction of decaboran(13)ate(-1), $B_{10}H_{13}^{-1}$, *J. Am. Chem. Soc.* 89 (1967) 5568–5573.
- 26 [34] C. Grimmer, M. Grandi, R. Zacharias, B. Cermenek, H. Weber, C. Morais, T.W.
27 Napporn, S. Weinberger, A. Schenk, V. Hacker, The electrooxidation of borohydride: A
28 mechanistic study on palladium (Pd/C) applying RRDE, ^{11}B -NMR and FTIR, *Appl. Catal.*
29 *B: Env.* 180 (2016) 614–621.

- 1 [35] E. Sanli, B.Z. Uysal, M.L. Aksu, The oxidation of NaBH_4 on electrochemically treated
2 silver electrodes, *Int. J. Hydrogen Energy* 33 (2008) 2097–2104.
- 3 [36] M. Chatenet, F. Micoud, I. Roche, E. Chainet, Kinetics of sodium borohydride direct
4 oxidation and oxygen reduction in sodium hydroxide electrolyte: Part I. BH_4^- electro-
5 oxidation on Au and Ag catalysts, *Electrochim. Acta* 51 (2006) 5459–5467.
- 6 [37] G. Rostamikia, M.J. Janik, Direct borohydride oxidation: mechanism determination and
7 design of alloy catalysts guided by density functional theory, *Energy Environ. Sci.* 3
8 (2010) 1262–1274.
- 9 [38] G. Rostamikia, R.J. Patel, I. Merino-Jimenez, M. Hickner, M.J. Janik, Electrocatalyst
10 design for direct borohydride oxidation guided by first principles, *J. Phys. Chem. C* 121
11 (2017) 2872–2881.
- 12 [39] D. Duan, H. Liu; Q. Wang, Y. Wang, S. Liu, Kinetics of sodium borohydride direct
13 oxidation on carbon supported Cu-Ag bimetallic nanocatalysts, *Electrochim. Acta* 198
14 (2016) 212–219.
- 15 [40] B. Molina Concha, M. Chatenet, Direct oxidation of sodium borohydride on Pt, Ag and
16 alloyed Pt–Ag electrodes in basic media. Part I: Bulk electrodes, *Electrochim. Acta* 54
17 (2009) 6119–6129.
- 18 [41] U.B. Demirci, Direct liquid-feed fuel cells: Thermodynamic and environmental concerns,
19 *J. Power Sources* 169 (2007) 239–246.
- 20