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# 1 Alkaline aqueous solution of sodium decahydro-*closo*- 2 decaborate Na<sub>2</sub>B<sub>10</sub>H<sub>10</sub> as liquid anodic fuel

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11

## 12 Abstract

13 The potential of the decahydro-*closo*-decaborate anion B<sub>10</sub>H<sub>10</sub><sup>2-</sup> 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 NaB<sub>10</sub>H<sub>10</sub> was first synthesized, fully  
16 characterized and assessed for its relative stability in alkaline medium for 25 days. Then,  
17 oxidation of B<sub>10</sub>H<sub>10</sub><sup>2-</sup> 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 B<sub>10</sub>H<sub>10</sub><sup>2-</sup>. A current density of *e.g.* 15.1 mA cm<sup>-2</sup> 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<sub>7</sub>-based anions for both silver and gold. Such results  
23 suggest the occurrence of partial oxidative degradation of B<sub>10</sub>H<sub>10</sub><sup>2-</sup> 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  $\text{NaBH}_4$ , 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  $\text{BH}_4^-$ , it spontaneously hydrolyzes when put into contact with water, which results in hydrogen evolution [9]:



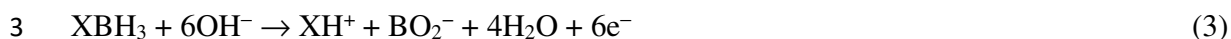
The reaction can be drastically limited by increasing the solution pH up to 10-13 [10]. The as-obtained alkaline aqueous solution of  $\text{BH}_4^-$  is then an attractive anodic fuel ( $E^\circ = -1.24 \text{ V}$ ) [11]:



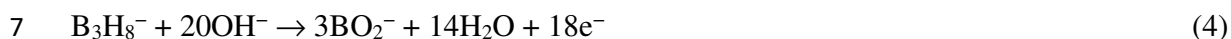
The resulting open circuit potential is as high as 1.64 V. A lot of efforts have been made to develop the related direct borohydride fuel cell technology but the progression objectives have been impeded by several critical issues [12]. One of the main problems relates to the unwanted hydrolysis reaction. 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  $\text{BH}_4^-$  an eight- or near-eight-electron process [15].

Alternatively, other boron hydrides, most being derivatives of  $\text{NaBH}_4$  [2], have been considered. For example, oxidations of alkaline aqueous solutions of ammonia borane  $\text{NH}_3\text{BH}_3$ , 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 N<sub>2</sub>H<sub>4</sub>(BH<sub>3</sub>)<sub>2</sub> over carbon-supported platinum and palladium nanoparticles were investigated and  
2 the boranes were compared each other [16]:



4 where X is equal to NH<sub>3</sub>, N<sub>2</sub>H<sub>4</sub> and NH(CH<sub>3</sub>)<sub>2</sub>. For each of the boranes, oxidation is in  
5 competition with heterogeneous hydrolysis, the H<sub>2</sub> evolution being more important over the  
6 platinum electrode. Another potential boron hydride is the octahydrotriborate anion B<sub>3</sub>H<sub>8</sub><sup>-</sup> [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 B<sub>12</sub>H<sub>12</sub><sup>-</sup> 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 B<sub>11</sub>H<sub>11</sub>O(OH)<sup>-</sup> and its formation was tentatively  
15 suggested to take place as follows:



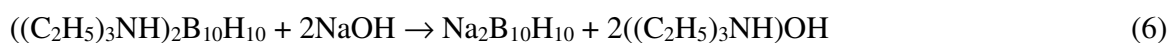
17 The most attractive feature with B<sub>12</sub>H<sub>12</sub><sup>-</sup> is the absence of heterogeneous hydrolysis. The  
18 evolving electrons are all due to partial oxidation of the anion.

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 B<sub>10</sub>H<sub>10</sub><sup>2-</sup> because, after the anion  
23 B<sub>12</sub>H<sub>12</sub><sup>2-</sup>, it is the second most stable species against hydrolysis [18]. The sodium salt, *i.e.*  
24 Na<sub>2</sub>B<sub>10</sub>H<sub>10</sub>, 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 B<sub>10</sub>H<sub>10</sub><sup>2-</sup> with platinum,  
27 gold and silver bulk electrodes.

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## 2. Material and Methods

$\text{Na}_2\text{B}_{10}\text{H}_{10}$  was prepared from the commercially available triethylammonium decahydro-*closo*-decaborate of formulae  $((\text{C}_2\text{H}_5)_3\text{NH})_2\text{B}_{10}\text{H}_{10}$  (Katchem, 98%) by cationic substitution in alkaline medium:



The synthesis was performed under argon atmosphere. A 2-gram aliquot of  $((\text{C}_2\text{H}_5)_3\text{NH})_2\text{B}_{10}\text{H}_{10}$  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  $\text{Na}_2\text{B}_{10}\text{H}_{10}$  was recovered by water extraction under vacuum.

The molecular structure of  $\text{Na}_2\text{B}_{10}\text{H}_{10}$  was analyzed by Fourier-transform infrared spectroscopy (FTIR; Nicolet™ IS50 Thermo Fisher Scientific; 32 scans), nuclear magnetic resonance (NMR; Bruker AVANCE-300;  $^1\text{H}$  such as probe head dual  $^1\text{H}$ , 300.13 MHz,  $\text{CD}_3\text{CN}$ , and 30 °C;  $^{11}\text{B}$  such as probe head BBO10, 79.39 MHz,  $\text{D}_2\text{O}$ , 30 °C). The crystal structure of  $\text{Na}_2\text{B}_{10}\text{H}_{10}$  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  $\text{Cu-K}\alpha_1$ :  $\lambda = 1.54059 \text{ \AA}$ . The thermal stability of  $\text{Na}_2\text{B}_{10}\text{H}_{10}$  was analyzed by thermogravimetric analysis (TGA; TA Instruments Q500; aluminum crucible of 40  $\mu\text{L}$ , heating rate 5°C min<sup>-1</sup>, under  $\text{N}_2$  flow of 60 mL min<sup>-1</sup>) as well as differential scanning calorimetric (DSC; TA Instruments 2920 MDSC; conditions identical to the TGA experiment).

The oxidation of the anion  $\text{B}_{10}\text{H}_{10}^{2-}$  (of  $\text{Na}_2\text{B}_{10}\text{H}_{10}$  in aqueous solution) was studied by cyclic voltammetry (with a  $\mu\text{Autolab}^{\text{®}}$  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  $\text{H}_2\text{SO}_5$  (Caro's Acid). Outgassed Milli-Q Water (18.2 M $\Omega$  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  $\varnothing$  2 mm, or bulk gold  $\varnothing$  2 mm, or bulk silver  $\varnothing$  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  $\text{BH}_4^-$  [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  $\text{BH}_4^-$ . 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 ( $0.25 \text{ mL min}^{-1}$ )  
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  $\text{N}_2$ . For detection, the conditions were: capillary potential of  
15  $3.5 \text{ kV}$ ; cone potential of  $30 \text{ V}$ ; source temperature at  $120^\circ\text{C}$ ; desolvation temperature at  $450^\circ\text{C}$ ;  
16 cone gas flow of  $50 \text{ L h}^{-1}$ ; desolvation gas flow of  $450 \text{ L h}^{-1}$ . 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.  
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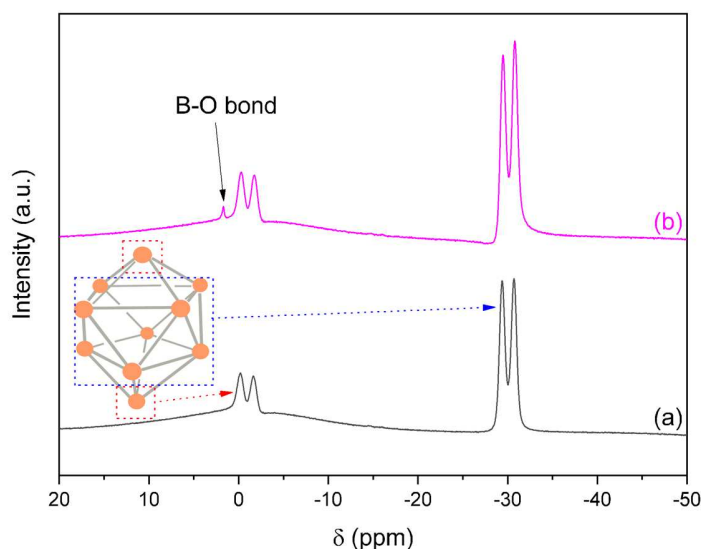
## 22 3. Results and discussion

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

24 The  $^{11}\text{B}$  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  $^1\text{H}$  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  $\text{H}_2\text{O}$  and to  $\text{CH}_3\text{CN}$  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



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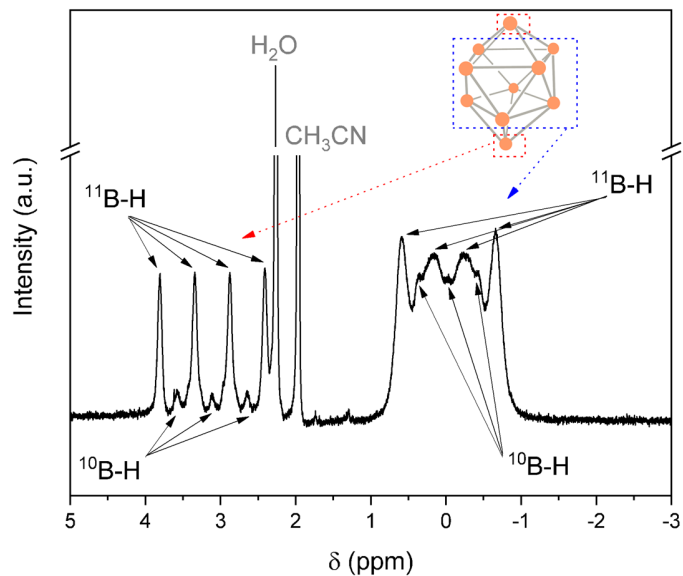
10 **Figure 1.** (a)  $^{11}\text{B}$  NMR spectrum of the anion  $\text{B}_{10}\text{H}_{10}^{2-}$  (from  $\text{Na}_2\text{B}_{10}\text{H}_{10}$ ). (b)  $^{11}\text{B}$  NMR spectrum of the anion  $\text{B}_{10}\text{H}_{10}^{2-}$  in an alkaline  
11 solution (1 M NaOH) after 25 days.

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  $2461\text{ cm}^{-1}$  are favorably ascribed to stretching of the apical and equatorial  
15 B–H bonds respectively. The bands between  $1300$  and  $1050\text{ cm}^{-1}$  are due to the B–H bonds  
16 deformation. The B–B bonds are featured by the band peaking at  $1026\text{ cm}^{-1}$ . 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  $3600\text{--}3500$  and  $1604\text{ cm}^{-1}$  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.



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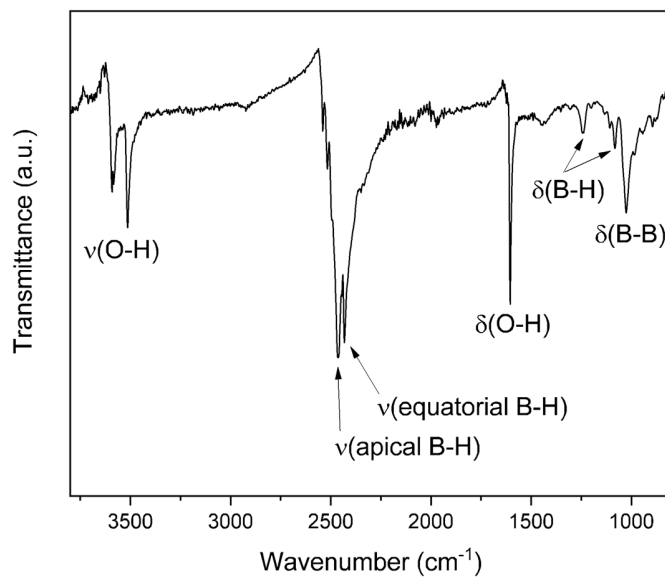
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**Figure 2.**  $^{11}\text{H}$  NMR spectrum of the anion  $\text{B}_{10}\text{H}_{10}^{2-}$  (from  $\text{Na}_2\text{B}_{10}\text{H}_{10}$ ).

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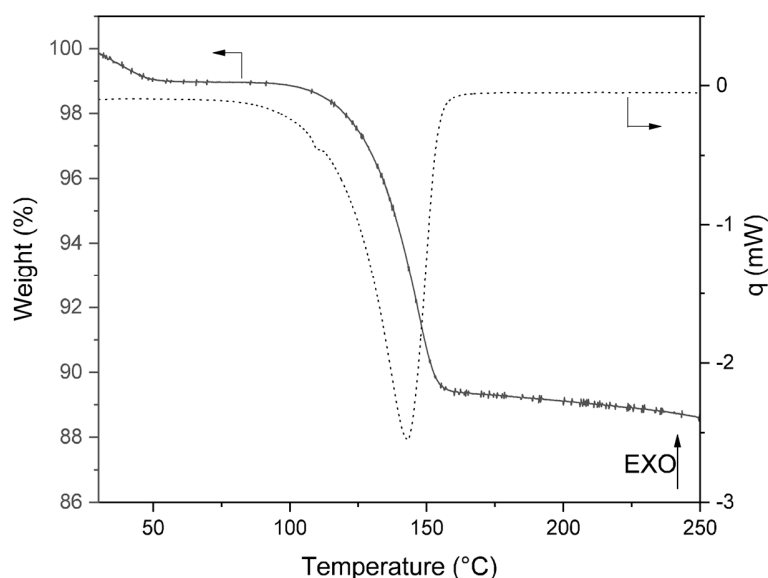
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**Figure 3.** FTIR spectrum of  $\text{Na}_2\text{B}_{10}\text{H}_{10}$ .

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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  $50^\circ\text{C}$  and a second one, more important (9.6 wt%), between  $100$  and  $160^\circ\text{C}$ . 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  $\text{Na}_2\text{B}_{10}\text{H}_{10}\cdot\text{H}_2\text{O}$ .

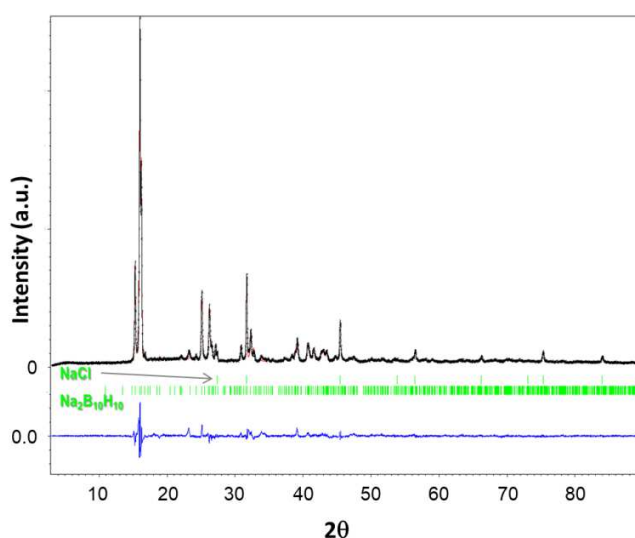


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Figure 4. TGA and DSC results for  $\text{Na}_2\text{B}_{10}\text{H}_{10}$ .

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  $110^\circ\text{C}$   
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  $2\theta$  range  $5^\circ$ - $100^\circ$  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  $\text{NaCl}$  ( $a = 5.639(1) \text{ \AA}$ , 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  $2\theta$ .

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

1 being analyzed once more by  $^{11}\text{B}$  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  $\text{B}_{20}$ -based polynuclear borane anions  
11 [29]. Another example is about oxidation by  $\text{MnO}_4^-$  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  $\text{BH}_4^-$   
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  $\text{H}_{\text{ads}}$ , 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.

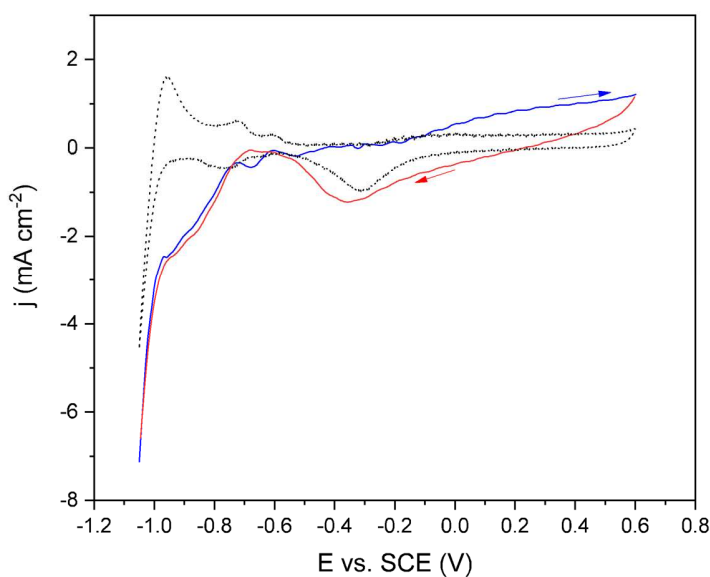
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### 26 3.4. Oxidation of $\text{B}_{10}\text{H}_{10}^{2-}$ over gold

27 Gold has been much investigated as effective electrode for oxidation of a boron hydride like  
28  $\text{NaBH}_4$  [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 ( $\text{H}_{\text{ads}}$ ) [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  $3.5 \text{ mA cm}^{-2}$ . 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 ( $0.7 \text{ mA cm}^{-2}$ ). 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  $4 \text{ mA cm}^{-2}$  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



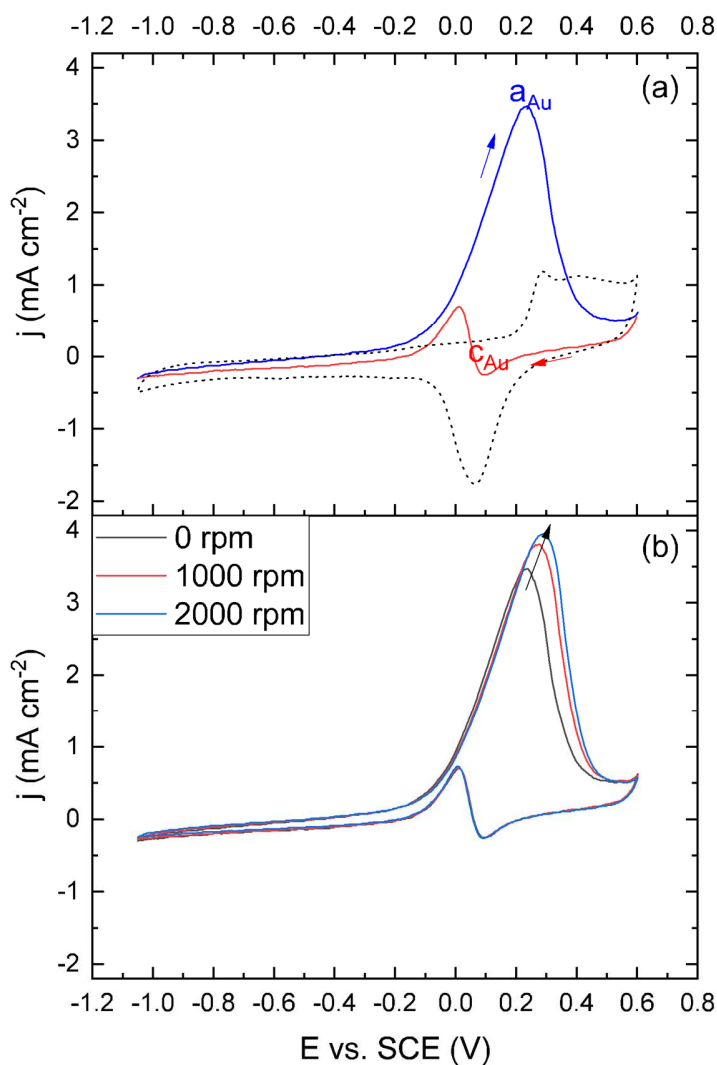
12

13 **Figure 6.** Cyclic voltammogram obtained on bulk platinum at  $100 \text{ mV s}^{-1}$  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<sup>-1</sup> 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 Na<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (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<sup>-1</sup> 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 B<sub>10</sub>H<sub>10</sub><sup>2-</sup> (118 g mol<sup>-1</sup>). One of them ( $m/z = 99.3$ ) was found to be predominant  
12 and it may be ascribed to B<sub>7</sub>H<sub>8</sub>O<sup>-</sup>. It is followed by the  $m/z$  value of 102.3, possibly due to

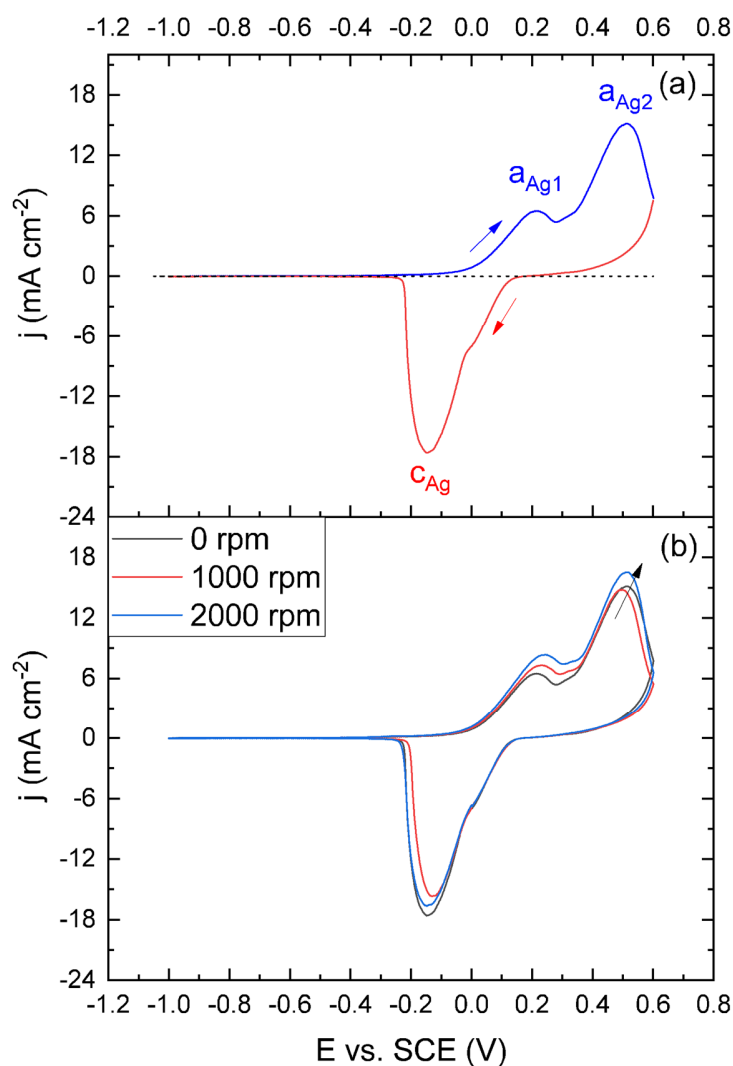
1  $B_7H_{11}O^-$ . The others were in fact detected in much lesser amounts and their identification has  
2 been difficult: the  $m/z$  values of 100.4 and 116.7 suggest species containing 7 boron atoms (*e.g.*  
3  $B_7H_9O^-$  and  $B_7H_9O_2^-$ ); and the  $m/z$  values of 69 might be ascribed to a species with 4 boron  
4 atoms (*e.g.*  $B_4H_{10}O^-$ ). 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  $B_{10}H_{10}^{2-}$ .

6

### 7 3.5. Oxidation of $B_{10}H_{10}^{2-}$ 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  $B_{10}H_{10}^{2-}$  [32]. With respect to the  
12 second oxidation wave, it may be also attributed to direct and possibly more complete oxidation  
13 of  $B_{10}H_{10}^{2-}$  [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  $BH_4^-$ , silver oxide was  
16 reported to be the electroactive surface responsible of the direct oxidation of the adsorbed  
17 intermediate  $BH_3OH^-$  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  $B_{10}H_{10}^{2-}$  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  $B_{12}H_{12}^{2-}$  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  $100 \text{ mV s}^{-1}$  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  $100 \text{ mV s}^{-1}$  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.*  $15.1 \text{ mA cm}^{-2}$  at  $0.51 \text{ V vs. SCE}$ ) 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

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27 cyclic voltammetry.

28

29

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