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# Sodium borohydride and propylene glycol, an effective combination for the generation of 2.3 wt% of hydrogen

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## ABSTRACT

Sodium borohydride  $\text{NaBH}_4$  (SB) readily and completely reacts with four equivalents of propylene glycol  $\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_3$  (PG), resulting in the liberation of four equivalents of  $\text{H}_2$  at temperatures starting from 25 °C. Alcoholysis (or glycolysis) takes place. The system SB-4PG is then an attractive  $\text{H}_2$  generator thanks to an effective gravimetric hydrogen storage capacity of 2.3 wt%. It offers several other advantages: there is no need of catalyst; there is no precipitation of by-product; PG is among the safest alcohols (much safer than e.g. methanol). The potential of SB-4PG as  $\text{H}_2$  generator is thus illustrated and discussed herein.

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## Introduction

The 21st Conference of the Parties of the United Nations Framework Convention on Climate Change through the Paris Climate Agreement is a turning-point in the worldwide awareness of global warming and its urgent mitigation [1]. For many years now fossil fuels have been identified as one of the major sources of the most abundant greenhouse gas, i.e. carbon dioxide. A lever for mitigating global warming is to develop sustainable and/or renewable energies as substitutes of fossil fuels, and several solutions have evolved in the past decades [2]. One of them is hydrogen [3].

Hydrogen (as a molecule) is a great opportunity in the field of sustainable and/or renewable energies but, because of some of its properties, the development of the so-called *near-future hydrogen economy* faces scientific and technical challenges. The state of the art shows three main challenges. (i) Hydrogen (as an atom) is abundant on earth, and *de facto* is found combined to other elements like carbon and oxygen. The molecule, which is a gas under normal conditions, has to be produced from sources like methane and water [4]. (ii) The gaseous state raises storage and distribution issues in terms of safety and energy density. Hence, classical (compression and cryogenics) and new (based on liquid or solid materials) storage solutions have been developed [5]. (iii) Hydrogen is mainly

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viewed as an energy carrier, which means that the chemical energy of the H–H bond ( $D = 436 \text{ kJ mol}^{-1}$ ) is expected to be converted into electrical energy. The convertor is the fuel cell technology [6].

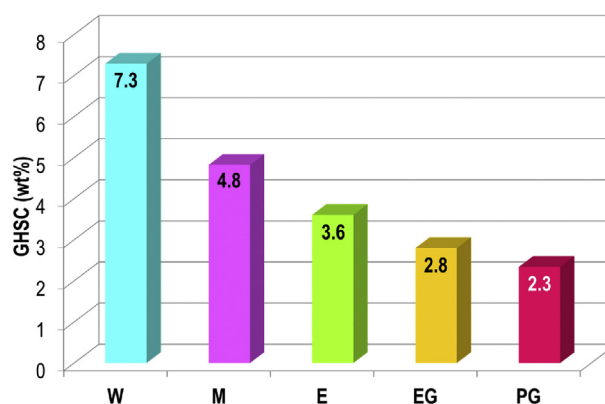
In the recent years the field of hydrogen storage has been decidedly dynamic resulting in the development of an impressive number of (old and new) materials that fall into two categories. The first category includes porous materials (e.g. metal organic frameworks, carbonaceous hosts, polymers with intrinsic porosity) that are able to reversibly store  $\text{H}_2$  at sub-zero temperatures. This is named physical  $\text{H}_2$  storage [7]. The second category regards chemical H storage, that is, materials where H is bound to a heteroatom like boron, magnesium, aluminum or a transition metal. They attractively offer high gravimetric/volumetric H storage capacities, but for most them storage is only partially reversible or even irreversible [8]. One example of chemical H storage material is sodium borohydride  $\text{NaBH}_4$ .

Sodium borohydride is an old material, discovered in the 1940s and which offers 10.8 wt% of hydridic hydrogens  $\text{H}^{\delta-}$  capable of spontaneously reacting with protic hydrogens  $\text{H}^{\delta+}$  coming from sources like water or alcohols (ROH) [9]. In these conditions, both  $\text{NaBH}_4$  and water (or an alcohol) are H carriers and  $\text{H}_2$  sources. Hydrolysis of  $\text{NaBH}_4$  has been studied extensively over the past 15 years, with a special focus on the catalytic materials [10]. Research is nowadays much more applied than in the past. There are experimental prototypes [11–13] and even commercialized devices [14–16]. Of important note is that the weak development of the catalytic hydrolysis of  $\text{NaBH}_4$  is directly related to the regeneration inefficiency of the spent hydrolysis fuel [5,8,14,16,17].

Alcoholysis of  $\text{NaBH}_4$  has been also explored, but in a lesser extent. Several alcohols have been examined so far. With methanol  $\text{CH}_3\text{OH}$ , the conversion of  $\text{NaBH}_4$  is complete [18], and the reaction is more efficient than hydrolysis [19,20]. Improved methanolysis kinetics takes place in the presence of (perchloric or boric) acids [21], metal catalysts (e.g. Pt–LiCoO<sub>2</sub>, CoCl<sub>2</sub>, NiCl<sub>2</sub>, Ni<sub>2</sub>P/SiO<sub>2</sub>) [22–24] and poly (ethylene imine) microgels [25]. Ethanol  $\text{C}_2\text{H}_5\text{OH}$  also reacts with  $\text{NaBH}_4$  but the kinetics of ethanolysis is 70 times slower than for methanolysis [18]. Accelerated reaction was reported in the presence of catalysts (acids and metal chlorides) [26] as well as for catalyzed ethanol-water mixtures [27]. Two other alcohols, i.e. isopropanol  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$  and *tert*-butanol  $\text{CH}_3\text{C}(\text{CH}_3)(\text{OH})\text{CH}_3$ , were found to be rather inert towards  $\text{NaBH}_4$  [18]. A last example of reactive alcohol is ethylene glycol  $\text{HOCH}_2\text{CH}_2\text{OH}$ , which can be used pure [28] or mixed with water [29].

At first sight, hydrolysis of  $\text{NaBH}_4$  may be seen as being superior to alcoholysis for two reasons: abundance of water and higher gravimetric hydrogen storage capacities (Fig. 1). However, a further comparison highlights clear benefits of using alcohols instead of water: i.e. potential for utilization in cold conditions (low freezing point), easy handling and efficient regeneration options for the spent fuels, and lower vapor pressure than water for the heavier alcohols [18–29]. In other words, there is a real interest in investigating various  $\text{H}^{\delta+}$  carriers in order to provide some options for the release of  $\text{H}_2$  from  $\text{NaBH}_4$ .

Propylene glycol  $\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_3$  ( $\text{C}_3\text{H}_8\text{O}_2$ ) appeals to alcoholysis of  $\text{NaBH}_4$ . An advantage of this diol is that it is



**Fig. 1 – Theoretical gravimetric hydrogen storage capacity (GHSC) of the couples  $\text{NaBH}_4\text{-}4\text{X}$  (with  $\text{X} = \text{W, M, E, EG}$  and  $\text{PG}$ , namely water, methanol, ethanol, ethylene glycol and propylene glycol, respectively). The couple  $\text{NaBH}_4\text{-}4\text{X}$  implies a stoichiometry where 1 mol of  $\text{NaBH}_4$  reacts with 4 mol of  $\text{X}$  resulting in the release of 4 mol of  $\text{H}_2$ . The capacity is calculated by dividing the molecular weight of  $4\text{H}_2$  molecules by the sum of the molecular weights of one equivalent of  $\text{NaBH}_4$  ( $37.8 \text{ g mol}^{-1}$ ) and 4 equivalents of  $\text{X}$ .**

quite safe. It is for instance much less toxic than methanol. It is besides comparable to water in terms of density ( $1.036 \text{ vs. } 1 \text{ g cm}^{-3}$ ). Otherwise, the theoretical gravimetric hydrogen storage capacity of the couple  $\text{NaBH}_4\text{-}4\text{C}_3\text{H}_8\text{O}_2$  (Fig. 1) is adequate (even relatively high) when it is compared to the capacities reported so far in the field of hydrogen storage [5–8]. Other attractive features have been identified through the systematic work presented hereafter, where the under-investigated propylene glycol has been considered as the sole source of  $\text{H}^{\delta+}$ . The primary objectives of the work were thus as follows: (i) showing the potential of the couple  $\text{NaBH}_4\text{-}4\text{C}_3\text{H}_8\text{O}_2$  for chemical hydrogen storage via the catalyst-free alcoholysis of the borohydride; (ii) optimizing the gravimetric hydrogen storage capacity at  $25^\circ\text{C}$ ; (iii) collecting data in order to better understand the features of the alcoholysis reaction; and (iv) putting the advantages of the diol forward.

## Experimental

Sodium borohydride  $\text{NaBH}_4$  (Sigma–Aldrich) and propylene glycol  $\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_3$  ( $\text{C}_3\text{H}_8(\text{OH})_2$ ; Sigma–Aldrich) were used as received. The former chemical was opened, handled and stored in an argon filled glove box (MBraun M200B,  $\text{O}_2 < 0.1 \text{ ppm}$ ,  $\text{H}_2\text{O} < 0.1 \text{ ppm}$ ).

The alcoholysis reaction (i.e.  $\text{H}_2$  evolution experiment) was performed as follows. In the glove box,  $\text{NaBH}_4$  and a small magnetic rod were transferred in a Schlenk tube that was sealed with a septum. Out of the glove box, the tube was immersed in an oil bath kept at a constant temperature and connected to an inverted burette filled with blue-colored water. In hydrolysis, we use to place a cold trap between the tube and the burette to condensate water vapor; such a trap was also used for alcoholysis. At that point the experimental set-up was checked for tightness. The appropriate volume of

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