**4- Boron- and nitrogen-based materials for chemical storage of hydrogen (and anodic fuels)**

*Ubiquitous Borane Fuel Electrooxidation on Pd/C and Pt/C Electrocatalysts: Toward Promising Direct Hydrazine–Borane Fuel Cells*

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**Collaboration:** Université Grenoble Alpes, CNRS, Grenoble INP (Institute of Engineering Université Grenoble Alpes), LEPMI + IRCELYON, UMR 5256, CNRS-Université de Lyon

**Involved MCP researchers:** Umit B. Demirci

Carbon-supported platinum and palladium nanoparticles were studied toward the oxidation of several boranes (namely ammonia–borane (AB), dimethylamine–borane (DMAB), hydrazine–borane (HB), and hydrazine–bis-borane (HBB)); only palladium is capable to oxidize directly and efficiently these fuels, as platinum first decomposes the boranes and then valorizes the evolved H2 and adsorbed Had.

Changing the nature of the borane fuel enables modulation of the borane oxidation performances at palladium electrodes; the best compromise is reached with HB (HBB suffers safety issues, and AB and DMAB are poisoned by the "counter-fragment" and/or its electroinactivity for any electrooxidation reaction). As a result, with a Pd/C electrode, HB oxidation is possible at low potential (close to the theoretical value), which holds promise for direct alkaline fuel cell applications. The temperature, HB concentration, and palladium nanoparticle loading on the electrode have a remarkable effect, which shows that the “direct” electrooxidation of the borane fuel (BH3OR) or of its adsorbates may compete with its spontaneous catalytic decomposition/hydrolysis into H2 followed by electrooxidation of H2 (HOR). The study also highlights that the reactant time of residence influences the pathway and completion of the reactions. These results demonstrate that, using suitable electrocatalysts, well-structured electrodes, and adequate borane fuel, the BH3OR thermodynamic onset potential value and the theoretical number of electrons per fuel moiety (ne− = 10 in the case of HB, 6 for the borane fragment and 4 for the hydrazine one) can nearly be reached, at reasonably low anode potential, which paves the way toward optimization of direct HB fuel cell systems.

*Sodium borohydride for the near-future energy: a “rough diamond” for Turkey*

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Boron-based materials are potential solutions in the field of energy. They have been regarded as hydrogen storage materials, liquid fuels of direct liquid-fed fuel cells (DLFCs), electrolytes of battery, and/or energetic substances. A typical example is sodium borohydride (NaBH4). In sodium hydroxide-stabilized aqueous solutions, it is seen as an efficient H2 generator or a performing fuel of DLFCs. Actually, it plays a wider role; it is also the precursor of several boron-based materials of interest in the field of energy. In other words, it is indirectly considered for other energy applications, i.e. solid electrolytes of all solid-state batteries and hypergolic fuel. De facto sodium borohydride has become a key...
Material in the field of energy. This is discussed in the present article, and it is highlighted that sodium borohydride may be clearly seen as a “rough diamond” for Turkey.

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


**Collaboration:** ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France
**Involved MCP researchers:** Umit B. Demirci

Sodium borohydride NaBH₄ (SB) readily and completely reacts with four equivalents of propylene glycol HOCH₂CH(OH)CH₃ (PG), resulting in the liberation of four equivalents of H₂ at temperatures starting from 25°C. Alcoholysis (or glycolysis) takes place. The system SB-4PG is then an attractive H₂ 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 H₂ generator is thus illustrated and discussed herein.

**Nanosizing Ammonia Borane with Nickel: A Path toward the Direct Hydrogen Release and Uptake of B-N-H Systems**


**Collaboration:** School of Chemical Engineering, University of New South Wales, Sydney, NSW 2052, Australia
**Involved MCP researchers:** Umit B. Demirci

Ammonia borane (AB), with one of the highest hydrogen content (19.6 mass%), has attracted much attention as a potential hydrogen storage material. However, its complex and multistep thermal decomposition process has left the idea that AB can only be an irreversible hydrogen storage material. Herein, we demonstrate the potential of a novel nanosizing strategy in overcoming current drawbacks. By (a) successfully restricting the particle size of AB to the nanoscale (≈50 nm), and (b) discreetly encapsulating the synthesized nanosized AB particles within a nickel (Ni) matrix, AB showed unforeseen hydrogen reversibility along its decomposition path. Owing to the catalytic effect of Ni and the embedment of AB with the Ni matrix, this nanosizing approach reduced the hydrogen release temperature, suppressed the melting of AB and the production of volatiles by-products including diborane and borazine. But more remarkably, this approach enabled the reversible release and uptake of pure hydrogen at 200 °C and 6 MPa H₂ pressure, only. Reversibility is thought to occur through an iminoborane oligomer resulting from the initial decomposition of the nanosized AB/Ni matrix. This result demonstrates for the first time the possibility of tailoring.
Robust 3D Boron Nitride Nanoscaffolds for Remarkable Hydrogen Storage Capacity from Ammonia Borane
Energy Technology 6 (2018) 570-577

Collaboration: Institute of Research on Ceramics (IRCER), UMR CNRS 7315, Centre Européen de la Céramique, Limoges (France)
Involved MCP researchers: Umit B. Demirci

Mesoporous monolithic (3D) boron nitride (BN) structures are synthesized using a template-assisted polymer-derived ceramic route. Polyborazylene is selected to impregnate monolithic activated carbon, which is used as template. After pyrolysis and template removal, this method supplies BN compounds with controlled crystallinity and tunable textural properties controlled by the temperature at which they have been annealed (from 1000 to 1450°C). Monoliths with an interconnected mesoporous network, high specific surface areas from 584 to 728 m² g⁻¹, significant pore volumes from 0.75 to 0.93 cm³ g⁻¹, and a relatively high compressive strength are generated. These highly porous compounds are used as nanoscaffolds to confine ammonia borane (AB). The composites provide an effective gravimetric hydrogen capacity of up to 8.1 wt%, based on AB measured at 100°C; this value demonstrates the high potential of this system as a safe potential hydrogen storage material.

About the Technological Readiness of the H₂ Generation by Hydrolysis of B(-N)-H Compounds
Energy Technology 6 (2018) 470-486

Collaboration: /
Involved MCP researchers: Umit B. Demirci

At the beginning of the new millennium, hydrolysis of sodium borohydride (NaBH₄) was presented as a promising on-board technology to generate H₂ for light-duty vehicles. Years later, other B(-N)-H compounds (e.g., lithium borohydride (LiBH₄) and ammonia borane (NH₃BH₃)) emerged as attractive alternatives whereas NaBH₄ was struggling with several issues jeopardizing its implementation. Actually, efforts in the research and development of H₂ generation by hydrolysis of B(-N)-H compounds have been intensive since the advent of NaBH₄ almost 20 years ago. There may be a question with respect to this: What is the technological readiness of the promising hydrolytic B(-N)-H compounds? This Review aims at providing relevant elements in response to this question. In the first part, the most mature B(-N)-H compounds are discussed at length. In the second part, a survey of all other candidates is proposed. It is concluded that NaBH₄ is the best hydrolytic B(-N)-H compound for marketing on a broad scale, but there are still key challenges to address.