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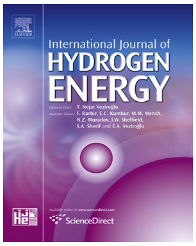

# Acid acceleration of hydrogen generation using seawater as a reactant

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ABSTRACT

The present study describes hydrogen generation from $NaBH_4$ in the presence of acid accelerator, boric oxide or $B_2O_3$, using seawater as a reactant. Reaction times and temperatures are adjusted using various delivery methods: bulk, addition funnel, and metering pump. It is found that the transition metal catalysts typically used to generate hydrogen gas are poisoned by seawater. $B_2O_3$ is not poisoned by seawater; in fact, reaction times are considerably faster in seawater using $B_2O_3$. Reaction times and temperatures are compared for pure water and seawater for each delivery method. It is found that using $B_2O_3$ with pure water, bulk addition is 97% complete in 3 min; pump metering provides a convenient method to extend the time to 27 min, a factor of 9 increase above bulk addition. Using $B_2O_3$ with seawater as a reactant, bulk addition is 97% complete in 1.35 min; pump metering extends the time to 23 min, a factor of 17 increase above bulk. A second acid accelerator, sodium bisulfate or $NaHSO_4$, is investigated here for use with $NaBH_4$ in seawater. Because it is non-reactive in seawater, i.e., no spontaneous $H_2$ generation, $NaHSO_4$ can be stored as a solution in seawater; because of its large solubility, it is ready to be metered into $NaBH_4$. With $NaHSO_4$ in seawater, pump metering increases the time to 97% completion from 3.4 min to 21 min. Metering allows the instantaneous flow rate of $H_2$, and reaction times and temperatures, to be tailored to a particular application. In one application, the seawater hydrogen generator characterized here is ideal for supplying $H_2$ gas directly to Proton Exchange Membrane fuel cells in sea surface or subsea environments where a reliable source of power is needed.

## Introduction

Metal hydrides are particularly useful for the generation of hydrogen gas whenever the use of compressed gas is inconvenient or unfeasible due to storage considerations. The metal hydrides lead in hydrogen-generating capacity per unit weight. Sodium borohydride, for example, reacts slowly with water, or more quickly in the presence of an accelerator, to liberate 4 moles of hydrogen gas per mole of the compound, or 2.6 L/g at room temperature:

$$NaBH_4 + 2H_2O(l) \xrightarrow{Accelerator} NaBO_2 + 4H_2(g) \quad \Delta H = -303.3\,kJ/mole \tag{1}$$

In addition to its large hydrogen generating capability, sodium borohydride has a number of advantages over the metals and other metal hydrides: (1) it is readily available in

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granular form at a moderate price, (2) it is stable for months in alkaline solution, (3) its solubility in water is high, and (4) it is relatively safe to handle, especially when it can be transported and stored in dry form.

Prior studies by Schlesinger and Brown describe the effect of acid accelerators and catalytic accelerators on the evolution of hydrogen gas from sodium borohydride using pure water as a reactant [1]. For the acid accelerators, they measure reaction times using a fixed ratio of acid to hydrogen-containing material (100 g accelerator:100 g $NaBH_4$). The amount of water used is limited by the ratio g $H_2O$:g $NaBH_4$ = 20:1. A US patent by Kerrebrock [2] describes hydrogen generation by hydrolysis of hydrides for undersea vehicle fuel cell energy systems. Hydrogen gas is generated from lithium borohydride using steam vaporized from pure water as an accelerator. Unlike the present study, Kerrebrock does not introduce seawater into the hydrogen generator as a reactant; seawater pumped in from the ocean is used only in the heat exchanger cooling coils. Only one reference [3] has been found for the generation of hydrogen gas using seawater as a reactant. In Ref. [3], Kliphuis uses sodium borohydride in combination with acid accelerator sodium bisulfate $NaHSO_4$ to create a pattern of bubbles which would simulate a wake. Acid is released in the water in the vicinity of the area where the sodium borohydride has been released. This is an open system allowing a continuous fresh supply of seawater to a moving reaction site. The ratio g $NaHSO_4$:g $NaBH_4$ is 5.1:6.6, or 77.3 g $NaHSO_4$ per 100 g $NaBH_4$. This ratio is far below the stoichiometric amount of accelerator required for complete reaction of the borohydride. Kliphuis indicates that generation of 30–50% of the theoretical yield of $H_2$ gas should be considered satisfactory.

## Methodology

### Chemicals

Cobalt doped sodium borohydride pellets were obtained from Sigma–Aldrich (90% $NaBH_4$, 7.5% $CoCl_2$). $H_2$ generation from one pellet is nominally 0.5 L. $NaBH_4$ in granular form was obtained from GFS (98%), $NaHSO_4$ from Acros Organics (99%), $CoCl_2$ from Sigma–Aldrich (97%), and $B_2O_3$ from Alfa Aesar (99%). Arrowhead distilled water was used. Seawater was collected from Pier 169 at SPAWAR Systems Center Pacific in San Diego and from Torrey Pines State Beach. No filtration of the seawater was performed.

### Experimental procedure

Three different experimental configurations, each with a different delivery method, are used in this study: (1) bulk, (2) addition funnel, and (3) peristaltic pump. A schematic of the bulk delivery configuration is shown in Fig. 1a. A Sigma–Aldrich 250 ml round bottom single neck flask with septum port is used as the reaction chamber (1). The gas evolved is collected in an inverted 4 L graduated cylinder above a water column (2). The temperature of the liquid in the reaction flask is monitored with a thermocouple puttied into the septum port (3), and the data recorded with a Lascar data logger (4).

When transition metal catalyst $CoCl_2$ is used, bulk delivery is accomplished by dropping commercially available pellets directly into the center neck of the reaction flask containing seawater or 35 parts per thousand (ppt) NaCl in place of seawater. When acid accelerator $NaHSO_4$ is used in place of a transition metal catalyst, bulk delivery is accomplished by dropping $NaBH_4$ granules into $NaHSO_4$ dissolved in seawater, or $NaBH_4$ dissolved in seawater is poured into $NaHSO_4$ dissolved in seawater. When acid accelerator $B_2O_3$ is used, $NaBH_4$ granules are dropped into $B_2O_3$ in seawater.

A schematic of the delivery funnel configuration is shown in Fig. 1b. An addition funnel (1) is set atop a Claisen tube (2) which fits into the reaction flask (3). The second arm of the Claisen tube (2a) feeds the evolved $H_2$ gas into a 4 L graduated cylinder (4). For the funnel experiments, only the $NaBH_4$/$B_2O_3$ combination is used. $NaBH_4$ dissolved in seawater (or water) (1) is added drop-wise to $B_2O_3$ in seawater (or water) (3). In this study, if there is a large disparity in solubility, the more soluble component is added to the less soluble component. $NaBH_4$, for example, is much more soluble in water (55 g/100 ml at 20 °C) than $B_2O_3$ (2.2 g/100 ml at 20 °C). This order of

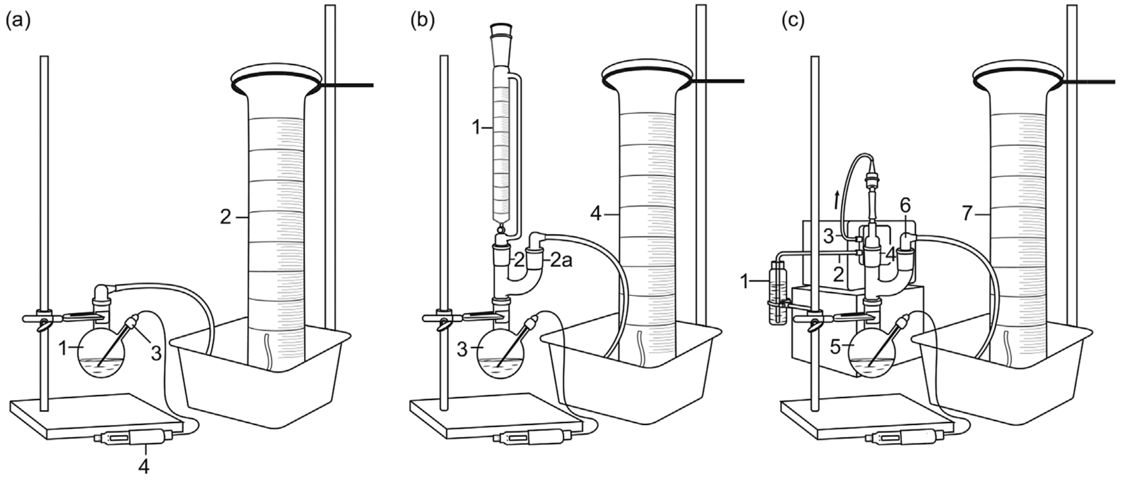

**Fig. 1 – Experimental configuration for (a) bulk, (b) addition funnel, and (c) peristaltic pump delivery.**