

## Recycling of sodium metaborate to borax

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### Abstract

This study investigated an electrochemical method for recycling sodium metaborate (NaBO<sub>2</sub>) to sodium borohydride (NaBH<sub>4</sub>). Palladium (Pd), boron-doped diamond (BDD), gold (Au) and platinum (Pt) were used as electrodes. Cyclic voltammetry and chronoamperometry were used to recycle the NaBO<sub>2</sub> either to NaBH<sub>4</sub> or to an intermediate material for making NaBH<sub>4</sub>. The electrochemical products were characterized by X-ray diffraction (XRD) as well as <sup>11</sup>B nuclear magnetic resonance (<sup>11</sup>Be NMR) and Fourier transform infrared (FT-IR) spectroscopy. Borax was generated preferentially on the Pd and BDD electrodes compared with Pt only at a constant potential of +1.54 V vs. Hg/HgO. An analysis of the XRD and FT-IR data clearly showed the formation of borax hydrate with a higher reactivity than NaBO<sub>2</sub>.

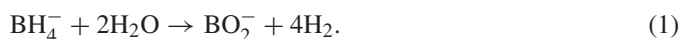
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### 1. Introduction

Sodium borohydride (NaBH<sub>4</sub>) was examined as a possible hydrogen storage material. NaBH<sub>4</sub> is more stable and non-flammable than other chemical hydrides and has a theoretical hydrogen content of approximately 10.6 wt%. Another advantage of NaBH<sub>4</sub> as a hydrogen storage material is that the hydrogen generation reaction occurs at room temperature and can be controlled by the amount of catalyst. Noble metals such as Ru/Pt and non-noble metals such as Co/Ni are generally used as catalysts for hydrogen evolution [1–5]. In addition, the possibility of NaBH<sub>4</sub> as a supply of hydrogen for fuel cells has been investigated [6].

The reaction between NaBH<sub>4</sub> and water generates hydrogen and metaborate [7]. The metaborate has a lower solubility than NaBH<sub>4</sub>, which decreases the hydrogen capacity of the fuel solution:



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The only disadvantage of using NaBH<sub>4</sub> as a hydrogen storage material is its cost. There are limited deposits of boron minerals used as raw materials for producing NaBH<sub>4</sub>, and it is difficult to convert the by-product (metaborate) to sodium borohydride. Therefore, in order to lower the overall cost of NaBH<sub>4</sub>, NaBO<sub>2</sub> needs to be recycled to NaBH<sub>4</sub>.

Various techniques for renewing borohydride from metaborate have been proposed. Cooper et al. reported the electrochemical conversion of NaBO<sub>2</sub> to NaBH<sub>4</sub> at room temperature and ambient pressure [8]. Kojima et al. reported other recycling processes employing thermal chemical methods [9]. NaBH<sub>4</sub> was synthesized from NaBO<sub>2</sub> with magnesium hydride (MgH<sub>2</sub>) under high temperatures (350–750 °C) and pressures (0.1–7 MPa). Li et al [10] recycled NaBO<sub>2</sub> to NaBH<sub>4</sub> using MgH<sub>2</sub>, as a reducing agent, and ball milling at room temperature.

Most studies have been performed under high temperatures and pressures, which involve considerable cost. Therefore, this study examined new reaction methods under milder conditions. The aim of this study was to reduce NaBO<sub>2</sub> to NaBH<sub>4</sub> by electrochemical methods in order to determine a way of recycling NaBO<sub>2</sub> to NaBH<sub>4</sub> or an intermediate material such as borax.

## 2. Experiment

### 2.1. Electrochemical experiments

A H-type conventional cell with an anolyte and catholyte separated by an anion exchange membrane (AMX, Neosepta) was used as the reactor. The role of the membrane was to prevent the diffusion of  $\text{Na}^+$ . The membrane maintained a high concentration of  $\text{BO}_2^-$  species near the anode. Gold (Au), palladium (Pd), platinum (Pt) (Sigma,  $25 \times 25 \times 0.5$  mm) and boron-doped diamond (BDD, Condias GmbH) were used as the working electrodes. The counter electrode was graphite ( $50 \times 80 \times 8$  mm). The reference electrode was Hg/HgO and all the experimental potentials reported were normalized to this reference electrode. An aqueous solution containing 20 wt% sodium metaborate ( $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ , Sigma) was used in all experiments, and the pH was 12.5 at  $25^\circ\text{C}$ .

The electrochemical experiments were controlled using an Autolab PGSTAT30. Cyclic voltammetry (CV) and chronoamperometry (CA) were used to examine the mechanisms of borate reduction. With CV, the scan rate was 50 and  $1 \text{ mV s}^{-1}$  ranging from  $-2.0$  to  $+2.0$  V and  $+1.0$  to  $+2.0$  V, respectively. The potential for CA was maintained at  $+1.54$  V for all working electrodes for a reaction time of 5 h.

For the BDD electrode, additional CA was performed to characterize the reaction. The potentials were  $+1.16$  and  $+1.89$  V, respectively, and the reaction time was 5 h. The white powder produced from the electrochemical experiments was washed with deionized water and dried in a dry oven at  $50^\circ\text{C}$  for 5 h.

Fig. 1 shows a schematic diagram of the process. The conceptual processes using hydrogen from  $\text{NaBH}_4$  consist of an electrochemical reactor, a  $\text{H}_2$  production cell, a polymer electrolyte fuel cell (PEMFC) and a power supply. Hydrogen is generated from an aqueous solution of  $\text{NaBH}_4$  with catalysts, and the PEMFC is operated by the hydrogen gas produced. After the hydrolysis of  $\text{NaBH}_4$ , sodium borate may be produced as a byproduct and be recycled to  $\text{NaBH}_4$  electrochemically in

a single step. All these steps are used for the ideal generation of hydrogen gas from the  $\text{NaBH}_4$  system.

### 2.2. Characterization

The white powder produced was examined by X-ray diffraction (XRD, Rigaku GmbH., Geigerflex D/MAX-II A, Germany), and Fourier transform infrared spectroscopy (FT-IR, Perkin-Elmer Ltd., Perkin-Elmer FT-IR spectrum GX, England). The XRD patterns were obtained at room temperature over a  $2\theta$  range of  $5^\circ$ – $90^\circ$  using filtered Cu  $K\alpha$  radiation (40 kV, 50 mA). A small amount of this white powder sample was mixed uniformly with KBr and pressed into pellets for FT-IR analysis. The transmittance spectra were recorded from 4000 to  $400 \text{ cm}^{-1}$  at a scanning number of 200.

The liquid phase samples reacting electrochemically were examined by horizontal attenuated total reflectance FT-IR (ATR FT-IR) spectroscopy and  $^{11}\text{B}$  nuclear magnetic resonance ( $^{11}\text{B}$  NMR, Bruker GmbH., Bruker model AMX-500, Germany) analysis. The ATR FT-IR spectra were obtained using same instrument in the case of the pellet used in FT-IR at a wavenumber range of  $4000$ – $750 \text{ cm}^{-1}$  and a scanning number of 200. The FT-IR spectra of the liquid samples were obtained using a horizontal model Spectra Tech ATR cell equipped with a  $45^\circ$  ZnSe trough plate. The  $^{11}\text{B}$  NMR spectra were obtained at room temperature at 500 MHz with an excitation pulse of  $0.85 \mu\text{s}$ . The chemical shift of  $^{11}\text{B}$  was referenced to a 15 wt%  $\text{BF}_3$  aqueous solution.

## 3. Results

### 3.1. Electrochemical analysis

Fig. 2 shows the cyclic voltammograms of the different working electrodes, Pd, Pt, Au and BDD in a 20 wt%  $\text{NaBO}_2$  aqueous solution. After CV at a scan rate of  $1 \text{ mV s}^{-1}$ , a small quantity of white powder was produced on the Pd and BDD

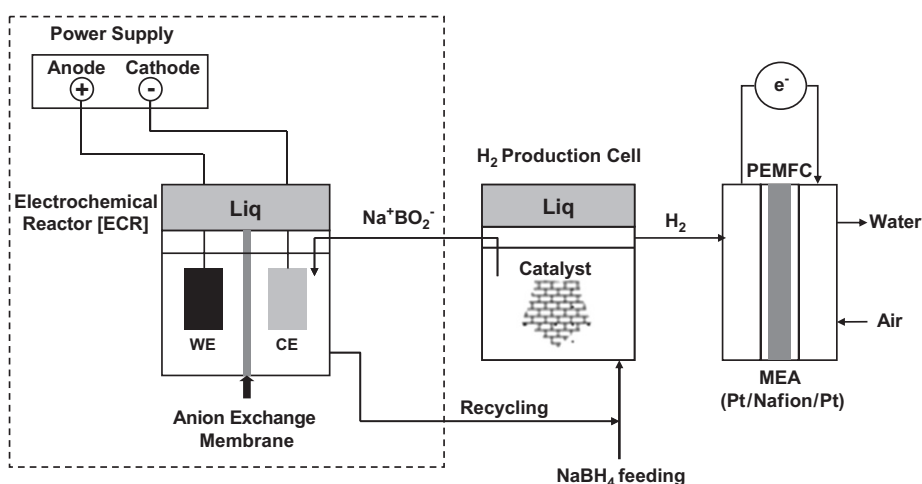


Fig. 1. An ideal schematic diagram for hydrogen generation from  $\text{NaBH}_4$  and recycling using electrochemical method.

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