



Short communication

Enhancement of electrocatalytic performance of hydrogen storage alloys by multi-walled carbon nanotubes for sodium borohydride oxidation



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HIGHLIGHTS

- High electrocatalytic performance, 500 mA cm⁻² at -0.3 V in 0.5 mol dm⁻³ NaBH₄.
- Hydrogen adsorption capacity of AB₅ was improved by the addition of MWNTs.
- Investigation for the role of MWNTs in NaBH₄ electrooxidation.

ARTICLE INFO

Article history:

Received 5 May 2013

Received in revised form

27 June 2013

Accepted 28 June 2013

Available online 6 July 2013

Keywords:

Hydrogen storage alloy

Multi-walled carbon nanotubes

Borohydride electrooxidation

Direct borohydride fuel cell

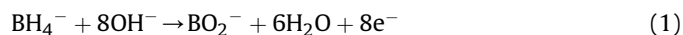
ABSTRACT

Catalytic electrodes consisting of MmNi_{0.58}Co_{0.07}Mn_{0.04}Al_{0.02} (AB₅-type alloy) and multi-walled carbon nanotubes (MWNTs) are studied for NaBH₄ electrooxidation and are characterized by scanning electron microscope and X-ray diffractometer. The NaBH₄ electrooxidation performance on the AB₅/MWNTs electrode is tested by cyclic voltammetry and chronoamperometry methods. The electrode performance is significantly affected by the content of MWNTs and the optimized content of MWNTs is found to be 2 wt.%. The steady state current density for NaBH₄ electrooxidation at the AB₅/MWNTs (2 wt.%) electrode is about twice of that at the AB₅ electrode without MWNTs. The utilization efficiency of NaBH₄ at the AB₅/MWNTs electrode is 61.5% higher than that at the pristine AB₅ electrode. The enhanced electrocatalytic activity and NaBH₄ utilization at the AB₅/MWNTs (2 wt.%) electrode can be attributed to MWNTs, which acts as a hydrogen adsorbent to diminish hydrogen release.

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1. Introduction

Direct borohydride fuel cells (DBFCs) have attracted much attention due to their high power density, high open circuit voltage, and low pollution [1–10]. As the fuel of DBFCs, NaBH₄ exhibits many advantages, such as, non-flammable, non-CO₂ emission, high hydrogen contents (10.6 wt.%), and high specific capacity (5668 Ah kg⁻¹). The complete electrooxidation of NaBH₄ generates 8 electrons (Eq. (1)). However, the hydrolysis (Eq. (2)) and the incomplete electrooxidation of NaBH₄ in alkaline solution lead to significant reduction in the utilization of NaBH₄ [1–12]. Therefore, it is necessary to develop electrocatalysts that can enhance the utilization of NaBH₄ by diminishing the hydrolysis and promoting the complete electrooxidation.



Electrocatalysts for borohydride oxidation usually includes precious metals and hydrogen storage alloys [12–29]. The precious metals have high catalytic activity, but they strongly catalyze the hydrolysis of borohydride (Eq. (2)) leading to the reduction of borohydride utilization and the decrease of the energy density of DBFCs [12–21]. Hydrogen storage alloys, on the other hand, have low catalytic activity for the borohydride hydrolysis and they also have the ability to absorb hydrogen formed by electrooxidation or hydrolysis of borohydride (Eqs. (3), (4)), so borohydride electrooxidation on hydrogen storage alloys usually has higher utilization than on precious metal catalysts. Besides, hydrogen storage alloys are cheaper than precious metals. However, the electrocatalytic activity of hydrogen storage alloys is much lower than precious metals.

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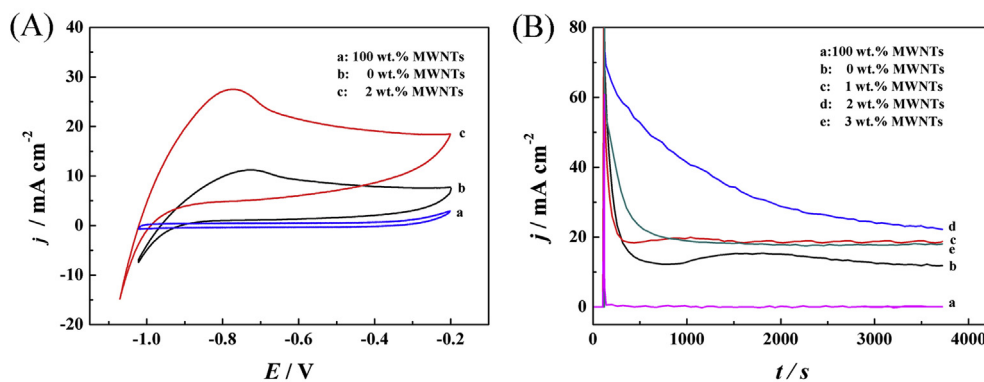
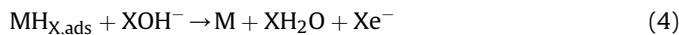
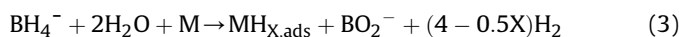


Fig. 1. Cyclic voltammograms of the MWNTs, AB₅ and AB₅/MWNTs (2 wt.%) electrodes in 0.1 mol dm⁻³ NaBH₄ + 2.0 mol dm⁻³ NaOH at a scan rate of 5 mV s⁻¹ (A) and chronoamperometric curves of the AB₅/MWNTs (x wt.%) in 0.1 mol dm⁻³ NaBH₄ + 2.0 mol dm⁻³ NaOH at -0.7 V (B).



In order to improve the catalytic performance of hydrogen storage alloys, surface modifications of hydrogen storage alloys have been studied. Wang et al. [24–26] investigated the modification of AB₅-type hydrogen storage alloys with Ti/Zr, Si and Au by ball-milling method. They found that hydrogen evolution was restrained on the hydrogen storage alloys with surface attached Ti/Zr or Si. However, the existence of Ti/Zr, Si and La₂O₃ decreased the catalytic activity for BH₄⁻ electrooxidation. Wang et al. [26] also found that doping the AB₅-type alloy with Au via a self-reduction method increased the BH₄⁻ electrooxidation current density from 100 to 175 mA cm⁻² in 1.0 mol dm⁻³ KBH₄. Our group [28,29] demonstrated that the surface modifications of AB₅-type alloy by Fe₂O₃ and Pd result in enhancements in their catalytic activity for BH₄⁻ electrooxidation.

Carbon nanotubes have been reported to be able to store hydrogen electrochemically and the stored hydrogen can be electrooxidized [30–32]. In this study, hydrogen storage alloy was combined with MWNTs to form a composite electrode. By taking the advantages of the electrochemical hydrogen storage ability and good electrical conductivity of MWNTs, the composite electrode achieved high catalytic activity for NaBH₄ electrooxidation and high NaBH₄ utilization. We provided evidences to illustrate that MWNTs plays a significant role in storing hydrogen and increasing hydrogen absorption in AB₅.

2. Experimental

The as-prepared MmNi_{0.58}Co_{0.07}Mn_{0.04}Al_{0.02} (AB₅-type alloy) was provided by Dandong Hongyuan alloy Co. Ltd. China, where Mm is the Mischmetal (an alloy of rare earth elements) consisting of Ce, La, Nd, Pr and trace amount of other elements. The MWNTs (10–20 nm in outer diameter and 5–15 μm in length) were purchased from Shenzhen Nanotech Port Co. Ltd.

The as-prepared AB₅-type alloy powder (400 mesh) was mixed with MWNTs at the mass ratio (Alloy:MWNTs) of 100:0, 99:1, 98:2, 97:3, respectively, in a solution containing 6 wt.% polytetrafluoroethylene (PTFE) and 1.5 wt.% sodium carboxymethyl cellulose (CMC). The mixture was smeared onto a Ni-foam sheet (10 × 10 × 1 mm) with a point-welded nickel wire as the current collector by a doctor-blade. After drying at 343.15 K for 2.5 h in a vacuum oven, the electrode was pressed under a pressure of 10 MPa. The thickness of the AB₅/MWNTs electrode is about 0.5 mm and the mass of the active material in an electrode is 0.2 g. All electrochemical experiments were carried out in a conventional three-electrode electrochemical cell with a carbon rod (3 mm in diameter) counter electrode and a saturated Ag/AgCl, KCl reference electrode. The system was controlled by a computerized potentiostat (Autolab PGSTAT302, Eco Chemie). All electrochemical measurements were conducted at room temperature under the protection of ultrapure N₂. All solutions were made with analytical grade chemical reagents and ultrapure water (Milli-Q, 18 MΩ cm).

The morphology of the electrodes was determined using a scanning electron microscope (SEM, JEOL JSM-6480). The structure was analyzed by a powder X-ray diffractometer (XRD, Rigaku TTR-III) equipped with Cu Kα radiation (λ = 0.15406 nm).

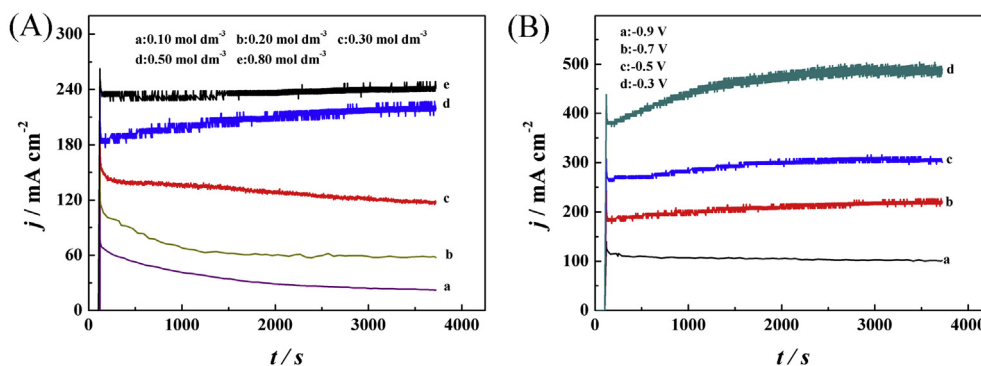


Fig. 2. Chronoamperometric curves of NaBH₄ electrooxidation at the AB₅/MWNTs (2 wt.%) electrode in 2.0 mol dm⁻³ NaOH + x mol dm⁻³ NaBH₄ at -0.7 V (A). Chronoamperometric curves of NaBH₄ electrooxidation at the AB₅/MWNTs (2 wt.%) electrode in 2.0 mol dm⁻³ NaOH + 0.5 mol dm⁻³ NaBH₄ at different potentials (B).

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