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High electrocatalytic activity of cobalt–multiwalled carbon nanotubes–cosmetic cotton nanostructures for sodium borohydride electrooxidation

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ABSTRACT

Flexible and wearable cobalt electrode with a unique three-dimensional hierarchical-network structure is prepared by electrodeposition of spherical Co particles onto multiwalled carbon nanotubes (MWNTs) which are assembled on the skeleton of cosmetic cotton (CC). The morphology and phase structure of the cobalt–multiwalled carbon nanotubes–cosmetic cotton (Co–MWNTs–CC) electrode are characterized by scanning electron microscope, transmission electron microscope and X-ray diffraction spectrometer. The $NaBH_4$ electrooxidation performance on the Co–MWNTs–CC electrode is investigated by means of cyclic voltammetry and chronoamperometry. Results show that the Co–MWNTs–CC electrode exhibits remarkably high catalytic activity and good stability for $NaBH_4$ electrooxidation. The oxidation current density reaches as high as 170 mA cm^{-2} at −0.7 V in 1.0 mol dm^{-3} NaOH and 0.1 mol dm^{-3} $NaBH_4$, which is higher than the most-related previous results.

Introduction

Direct borohydride fuel cells (DBFCs) using $NaBH_4$ directly as the fuel have attracted much attention recently. The advantages of $NaBH_4$ as a fuel include a high energy density (9.3 Wh g^{-1}), high hydrogen contents (10.6 wt.%), high chemical stability in alkaline solution, non-toxic, and easy handling [1–5]. The complete electrooxidation of $NaBH_4$ generates 8 electrons (Eq. (1)) [1–29]. During the past years, the catalytic electrooxidation of $NaBH_4$ has been widely studied using various catalysts. Noble metals such as Pd, Pt, Os, Au, Ag, and their alloys exhibited high catalytic activity [9–19]. However, they suffer a drawback of high cost. Transition metals such as Ni, Cu, Zn [20–24] and hydrogen storage alloys [24–29] are alternative low cost catalysts for $NaBH_4$ electrooxidation but they have lower catalytic activity than precious metal catalysts, and thus they are always combined with noble metals to improve the catalytic activity of the catalyst, such as Au–Cu, Au–Ni, Pt–Ni, $LaNi_{4.5}Al_{0.5}$-Au and so on [10,11,13,15,18,19,29]. Cobalt, another transition metal, is always employed to prepare alloy with noble metals to improve the performance, such as Pt–Co, Au–Co [13,18,19]. M.J. Janik pointed out that the electrooxidation of BH_4^- must result in the breaking of four B–H bonds [1]. D.M.F. Santos pointed out that Co has a stronger ability than other non-previous metals in breaking the B–H

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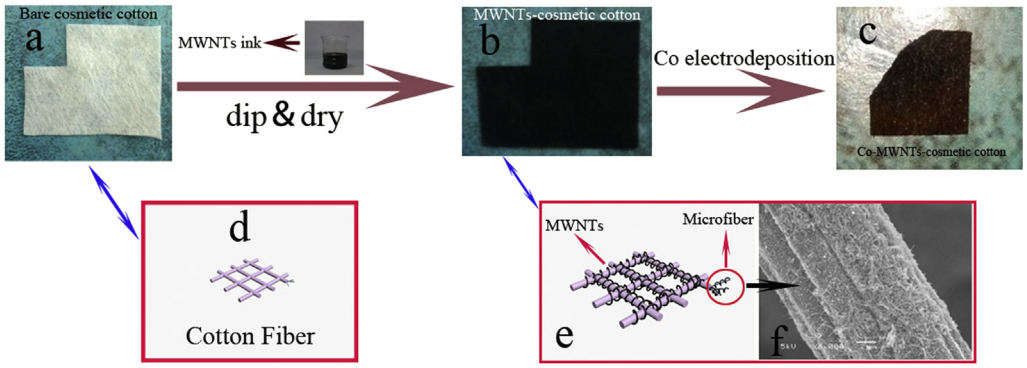

Fig. 1 – Fabrication process of Co–MWNTs–CC electrode.

bond [5], so we believe the Co will obtain a higher catalytic activity. However, few of report are about the pure cobalt for $NaBH_4$ electrooxidation. So improving the catalytic performance of the pure cobalt electrodes is significant for the development of low cost and high performance DBFCs. Besides, the study of the pure cobalt metal catalyst must be conducive to the study of the alloys containing cobalt for further.

$$BH_4^- + 8OH^- \rightarrow BO_2^- + 4H_2O + 8e^- \quad (1)$$

Recently, flexible electrodes have caught researchers' attention due to their portability and high deformability [30–36]. Recently, we fabricated a flexible Ni@MWNTs/Sponge electrode for $NaBH_4$ electrooxidation and achieved a high catalytic performance [36]. Carbon fiber cloth is usually used as the base structure of the flexible electrode due to its high conductivity and corrosion resistance [30–33]. Textile with carbon nanotubes (CNTs) was employed as the base of energy storage device [34], which was considered as a new flexible electrode material. However, few of these reports has been focus on DBFCs. Cosmetic cotton is another flexible material for fabrication of novel exciting and remarkable performance electrodes because cosmetic cotton is a deformable material with a hierarchical-network nature. Such a three-dimensional (3D) network allows large contact area between the active material and electrolyte. Besides, it is readily available and quite inexpensive.

In this paper, MWNTs, employed as a fine hydrogen storage material to improve the catalytic activity of $LaNi_5$ alloy for $NaBH_4$ electrooxidation in our previous work [26], were wrapped around the framework of CC via self-assembling to form a conductive hierarchical-netwok nanostructured substrate and then spherical Co particles were directly electrodeposited on the surface of MWNTs layer. The novel 3D nanostructured Co–MWNTs–CC electrode shows remarkably high catalytic activity and stability for $NaBH_4$ electrooxidation. The oxidation current density on Co–MWNTs–CC electrode is much higher than the reported transition metals electrodes, such as Zn, Ni and hydrogen storage alloys [23–29].

Experimental

The Co–MWNTs–CC electrodes were prepared by self-assembling of MWNTs layer on CC followed by electrodeposition of Co on conductive MWNTs surface. To prepare the MWNTs–CC substrate, a piece of CC (HAOLING Daily necessily & Cosmetics Co. Ltd.) was washed by acetone and ethanol for several times to get rid of greasy dirt and then dried at 373.15 K in a vacuum oven for 2 h prior to use.

The cleaned CC was dipped in a MWNTs suspension, which consists of 2.6 mg cm^{-3} MWNTs (>50 nm in outer diameter and 10–20 μm in length, Shenzhen Nanotech Port Co. Ltd.) and 10 mg cm^{-3} of sodium dodecyl benzene sulfonate (SDBS) and 50 mL ultrapure water (Milli-Q, 18 MΩ cm). The suspension was prepared by sonicating the mixture for 12 h at ambient temperature. After dipping for 30 s, the CC was removed from the suspension and dried at 373.15 K for 2 h. The dip–dry cycle was repeated once again to obtain the MWNTs–CC substrate, which were further washed with a large amount of ultrapure water to remove SDBS. The MWNTs–CC has a sheet resistance of 1Ω/square, measured by four points probe technique. Electrodeposition of Co on substrates was performed using Autolab PGSTAT302 (Eco Chemie) electrochemical work station in a conventional three-electrode electrochemical cell with a saturated Ag/AgCl, KCl reference electrode and Pt foil counter electrode. The electrodeposition was carried out at a constant current of 3 mA cm^{-2} for 4 h in the solution containing 2.5 mol dm^{-3} KCl, 0.4 mol dm^{-3} NH_4Cl, 0.5 mol dm^{-3} H_3BO_3 and 1.0 mol dm^{-3} $CoCl_2 \cdot 6H_2O$. $NaBH_4$ electrooxidation was also performed in the same three-electrode electrochemical cell using the 1 cm^2 Co–MWNTs–CC electrode.

The morphology of the electrodes was determined using a scanning electron microscope (SEM, JEOL JSM-6480) and a transmission electron microscope (TEM, FEI TeccaiG2S-Twin, Philips). The structure was analyzed by a powder X-ray diffractometer (XRD, Rigaku TTR- III) equipped with Cu Kα radiation ($\lambda = 0.15406$ nm).

Results and discussion

Fabrication process of Co–MWNTs–CC electrode

The fabrication process of the Co–MWNTs–CC electrodes and corresponding photos of the samples are shown in Fig. 1. The pure CC substrate is made up of cotton fibers which have a hierarchical structure with complicated surface morphology,

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