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Short Communication

Hydrogen generation from alkaline $NaBH_4$ solution using a dandelion-like Co–Mo–B catalyst supported on carbon cloth

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ABSTRACT

In this study, a dandelion-like Co–Mo–B catalyst was prepared on carbon cloth (CC) by two-step electrodeposition method for the first time. The composition and microscopy are characterized by XRD and SEM technology. The results revealed that the as-synthesized Co–Mo–B catalyst exhibited high hydrogen generation rate (1280.80 mL min^{-1} g^{-1}) and low activation energy (51.0 kJ mol^{-1}) for the hydrolysis of alkaline $NaBH_4$ solution. The results reveal that the reason might be due to high specific surface of the novel dandelion-like nanostructure and the synergistic effect of Co, Mo and B. Moreover, the catalytic activity was closely related to NaOH concentration, and OH^- anions were competitive with BH_4^- anions in alkaline $NaBH_4$ solution to transfer to the catalyst surface.

Introduction

Hydrogen is well known as clean and high efficiency energy source, which can meet the demands of low pollution and sustainable development. The pure hydrogen is ideal fuel for proton exchange membrane fuel cell (PEMFC). By the PEMFC, chemical energy can directly convert into electricity with the only byproduct of water [1]. Therefore, PEMFC has been

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considered as promising power source for portable electronic devices and automobiles because of its high power density, low operating temperature and simple structure. But so far hydrogen storage technologies are not convenient and reliable due to safety and economic issues. As a typical chemical hydride, sodium borohydride ($NaBH_4$) has been considered as a safe and convenient hydrogen source because of its high hydrogen storage capacity (10.8 wt%), non-toxicity, mild operation temperature and controllable hydrolysis reaction [2]. The pure hydrogen can be released by the presented catalysts for hydrolysis of alkaline $NaBH_4$ solution at room temperature according to the following reaction [3]:

$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2$ (1)

The reaction of the hydrolysis of $NaBH_4$ needs to be activated by various catalysts, mainly including noble metal and non-noble metal catalysts. Although platinum [4], rhodium [5], ruthenium [6] and corresponding noble metal alloys show good catalytic activity for the hydrolysis of $NaBH_4$, these noble metal catalysts are very expensive and the abundances are too limited to be widely applied. The non-noble metal catalysts such as cobalt, nickel, copper and their alloys (Co–B [7], Ni–B [8], Co–Mo–B [9], Co–Ni–B [10], Co–Ni–P [11]) are inexpensive and also show high catalytic activity for the hydrolysis of $NaBH_4$, even higher than that of some noble metal-based catalysts. Recently, Co–Mo–B catalysts are considered to be a good candidate as the catalyst for the hydrolysis of $NaBH_4$. However, traditional catalysts are usually prepared in the form of powder, which is easy to agglomerate and difficult to be reused. Above-mentioned issues restrict those applications in hydrogen generation reactors. To achieve well-dispersed catalysts, supported materials are adopted, which can be beneficial to increase the contact area between catalysts and reactants, and consequently improve the catalytic activity. Many materials like Cu sheet [12], Ni foam [13,14], γ-Al_2O_3 [15], and carbon cloth [16] and so on, have been reported as catalyst substrates in previous literature. Among them, carbon cloth (CC) shows a unique 3D network structure and is considered to be attractive for application because of its good flexibility and high electrical conductivity. But so far, it has been not chosen as the substrate of the catalyst for the hydrolysis of $NaBH_4$.

In this work, a dandelion-like Co–Mo–B catalyst is successfully synthesized on carbon cloth by two-step electrodeposition method for the first time, which has been characterized and verified by SEM and EDS analysis. We study the effect of different conditions (NaOH concentration, and solution temperature) on hydrolysis reaction and performance. The as-prepared Co–Mo–B catalyst exhibits high hydrogen generation rate (HGR) and low activation energy for the hydrolysis of $NaBH_4$.

Experimental

Carbon cloth was first immersed in ethanol absolute and washed using an ultrasonic for 30 min to remove the greasy dirt on the surface, and then soaked in 10 vol.% HCl solution for 5 min to remove inorganic impurities, cleaned by deionized water and dried at 50 °C for 12 h. Finally, the pretreated carbon cloth was weighted and stored for the following experiment. The detailed electrodeposition conditions were listed in Table 1. The preparation process is as follows: 1) The pretreated carbon cloth was plated in the No. 1 of coating bath for 20 min to deposit Co component. 2) Put the carbon cloth into the No. 2 of coating bath for 20 min to deposit Mo component. 3) During the procedure to prepare Co and Mo component, B has been deposited. Co, Mo and B component are the products of co-electroplating process. 4) The as-deposited Co–Mo–B catalyst was weighted to determine the weight of Co–Mo–B catalyst after being dried. The weight of the Co–Mo–B catalyst was determined according to the following equation:

$$m_{Co-Mo-B\ catalyst} = m_{Co-Mo-B/CC} - m_{CC} \quad (1)$$

where $m_{Co-Mo-B\ catalyst}$, $m_{Co-Mo-B\ catalyst}$ and m_{CC} represent the weight of Co–Mo–B catalyst, Co–Mo–B/CC sample and bare carbon cloth before depositing, respectively.

The hydrogen generation rate (HGR) was measured by classical water-displacement method [17] and calculated according to the amount of Co–Mo–B, excluding the weight of carbon cloth. It should be pointed out that the hydrolysis reaction of $NaBH_4$ is accorded with the characteristic of zero order reaction [3,6].

The composition of the Co–Mo–B catalyst was performed by conventional X-ray powder diffraction (XRD) on a Rigaku D/MAX-RB diffractometer (Rigaku, Japan) with Cu Kα radiation ($\lambda = 1.54178$ Å). Surface morphology of catalyst was studied by scanning electron microscopy (SEM, HITACHI S-4300, Japan) equipped with energy-dispersive spectroscopy analysis (EDS). The specific surface area was determined by Brunauer–Emmett–Teller (BET) nitrogen adsorption–desorption measurement (BELSORP-Mini).

Results and discussion

Catalyst characterization

The XRD patterns of commercial blank carbon cloth and as-prepared Co–Mo–B catalyst have been shown in Fig. 1. For the commercial blank carbon cloth, the broad peak centered at around 43.8° should be indexed to the (101) plane of carbon in carbon cloth (JCPDS card No: 75-1621), which is in good agreement with the literature reported [18]. Compared with the blank carbon cloth, it can be found that Co–Mo–B catalyst is a mixture of two phases, including MoB_2 and Co, except for the peak of the carbon cloth substrate. The diffraction peaks at 41.8°, 44.4°, 47.3°, 51.6°, 76.1° and 84.1° can be well assigned to the hexagonal Co phase (JCPDS card No: 1-1254). The small peak and sharp peak of MoB_2 phase (JCPDS card NO: 6-682) are detected at $2\theta = 33.9°$ and 45.3°, corresponding to the (100) and (101) planes, respectively.

The surface morphology of Co–Mo–B catalyst is further characterized by SEM in Fig. 2. From the low-magnification SEM image (Fig. 2a and b), it can be shown that the whole surface of the carbon cloth has been covered uniformly with