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Co(Fe)/MWCNT nanoelectrode for hydrogen storage applications

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Abstract

The electrochemical hydrogen discharge capacity of cobalt (iron)/multiwalled carbon nanotubes (MWCNTs) has been investigated and discussed in this study. Iron (cobalt) was electrochemically deposited on copper foam, and MWCNTs were added to the electrode via a dropwise method to create nanoelectrodes that serve as active anode materials for reversible hydrogen ion storage. The MWCNTs had previously been washed with acid to create active sites for hydrogen adsorption. After characterization, the discharge capacity of the nanoelectrodes was examined, revealing that the cobalt/MWCNT nanoelectrode exhibited a greater discharge capacity of 1320 mAh/gr compared to the iron/MWCNT nanoelectrode, which had a discharge capacity of 1210 mAh/gr at a constant current of 1 mA. Due to cobalt's lower electrical resistivity and greater stability compared to iron, cobalt-based nanoelectrodes demonstrate superior reduction activity and discharge capacity over their iron-based counterparts. Therefore, these nanoelectrodes are promising materials for hydrogen storage applications.

Keywords: Electrochemical hydrogen storage capacity, MWCNT, Cobalt nanoelectrode, Iron nanoelectrode.

1. Introduction

The demand for energy is growing, and the raw materials for the fossil fuel economy are diminishing. Oil, coal, and natural gas supplies are not replenished as they are consumed, necessitating the search for alternatives [1-4]. Hydrogen offers three fundamental benefits that address these concerns: its use significantly reduces pollution, and it can be produced locally from various sources. Hydrogen storage is a key enabling technology for advancing hydrogen and fuel cell technologies across multiple applications, including stationary power, portable power, and transportation [5]. Hydrogen has the highest energy per mass of any fuel; however, its low density at ambient temperature results in a low energy per unit volume, which necessitates the development of advanced storage methods with potential for higher energy density. Hydrogen can be stored physically as either a gas or a liquid. Storing hydrogen as a gas typically requires high-pressure tanks (350–700 bar or 5,000–10,000 psi). Conversely, storing hydrogen as a liquid necessitates cryogenic temperatures because the boiling point of hydrogen at one atmosphere pressure is −252.8 °C. Additionally, hydrogen can be stored on the surfaces of solids (by adsorption) or within solids (by absorption) [6-8]. Researchers have focused on improving hydrogen storage system technology and developing novel hydrogen storage materials. The primary solid hydrogen storage materials studied include carbon nanotubes (CNTs), metal hydrides, borohydrides, and aluminum hydrides [9-12]. In 1997, Dillon et al. first reported the high hydrogen storage capacity of single-walled carbon nanotubes (SWCNTs), achieving 5–10 wt% under the conditions of 273 K and 0.04 MPa, which could meet the hydrogen storage target set by the United States Department of Energy (US DOE); therefore, they considered CNTs to be an ideal hydrogen storage material. CNTs play an important role in energy storage devices, such as photovoltaic cells, supercapacitors, and lithium-ion batteries [14,15].

Thus, investigations of CNTs as candidate hydrogen storage materials will continue over the next few decades. The results of work with pristine unmodified CNTs have been somewhat disappointing, leading researchers to turn their attention to modified CNTs. This has led to a variety of investigations dealing with the modification of carbon materials, such as physical treatment, chemical treatment, loading various dopants (metals, metal oxides, hydrides, and heteroatoms), and exploring CNTs in various geometrical forms and phase purity.

It is generally acknowledged that modifying carbon nanostructures with metal atoms is an effective way to improve their hydrogen storage performance [16].

Table 1. Atomic percentage(A%) for elements in nanoelectrodes.

Element	Fe/MWCNT electrode	Co/MWCNT electrode
C	46.05	31.63
O	53.47	59.07
Fe	0.35	-------
Co	------	8.86

Common metals used for decorating carbon backbones include alkali metals [17] , alkaline earth metals [18], transition metals [19], and other simple metals [20].

In this study, multiwalled carbon nanotubes were applied using a dropwise method to cover cobalt (Co) or iron (Fe) deposited on a Cu foam electrode for use as an anode material to investigate the hydrogen storage capacity of the nanoelectrode.

2. Experimental details

2.1. Purification

Using a chemical vapor deposition technique (CVD) together with a molybdenum catalyst (Mo) [21], MWCNTs were synthesized for use in a dropwise method to create a homogeneous MWCNT layer on a Co(Fe)-Cu electrode. The surface treatment of the MWCNTs was carried out via sonication in a mixture of nitric acid and sulfuric acid (1:3 by volume) for 4 hours at 50 °C. The resulting MWCNTs were then thoroughly washed several times with deionized water until a solution with a pH of 7 was obtained. Finally, they were dried at 100 °C for 3 hours, allowing carboxylic functional groups (-COOH) to attach to the MWCNT surface, which caused them to be uniformly dispersed in the bath [22, 23].

2.2. Preparation of electrodes

The electroplating method was used to prepare a Co(Fe) layer on a small (1×1 cm^2) Cu foam with nanoscale porosity (as a frame). Before coating Co(Fe) on the Cu foam, the surface of the pure Cu foam was cleaned with acetone. The electroplating bath solution for the first sample (the Co layer on the Cu foam, named S1) consisted of 312 g L^{-1} $CoSO_4\cdot(H_2O)_2$, 6.19 g L^{-1} NaCl, and 100 g L^{-1} H_3BO_3, while the second sample (the Fe layer on the Cu foam, named S2) consisted of 298.2 g L^{-1} $FeCl_2$, 36.6 g L^{-1} $CaCl_2$, and HCl. Electroplating processes were conducted in electrochemical baths at 25 °C for the first sample and 50 °C for the second sample, with magnetic stirring at 300 rpm, a current density of 5 mA cm^{-2}, and a duration of 5 minutes. Notably, a Pt plate was used as the counter electrode (cathode), while Cu foam served as the working electrode (anode), separated by a gap of 1 cm. In this way, the Co(Fe) layer was coated onto the Cu foam surface. Subsequently, the MWCNTs and acetone were sonicated for 1 hour. Afterward, the MWCNTs were applied to both the first electrode (S1) and the second electrode (S2). Consequently, several layers of MWCNTs were placed on the electrodes to be used as active materials for investigating hydrogen storage capacity.

3. Results and discussion

Figure 1a and 1b show the X-ray diffraction (XRD) patterns of the Cu-Fe or Co/MWCNT nanoelectrodes, respectively. This figure indicates the presence of carbon in the hexagonal phase at 2θ ranging from 20° to 30°, while the other diffraction peaks indicate the presence of Fe, Fe-C, and Co in each nanoelectrode. In fact, there is a peak list beneath each figure that indicates the standard XRD card number and the crystallographic phase corresponding to each peak.

Figure 2a and 2b show the SEM micrographs of the surface morphologies of the Cu-Fe and Cu-Co MWCNT nanoelectrodes, respectively. The MWCNTs dispersed on each electrode can be clearly observed.

Figure 3 shows the EDX spectrum of (a) Fe/MWCNT and (b) Co/MWCNT nanoelectrodes. This spectrum confirms the presence of C, Fe (Co), and also indicates the presence of O and C in the MWCNTs (due to the functionalized MWCNTs), which suggests that the nanoelectrodes were properly synthesized. Table 1 demonstrates the atomic percentage (A%) of the elements present in the nanoelectrodes.

Discharge capacity (mAh/gr) = [constant current (mA) × discharge time (h)]/active material weight (gr)] (1)

In this study, H^+ ions were absorbed in the working electrode during the charging process, and their extraction from the working electrode was considered discharge based on the half-cell reaction. The hydrogen storage capacity was investigated by the number of discharge cycles. Figure 5a and 5b show the electrochemical discharge capacities of the S1 and S2 nanoelectrodes, respectively. This figure illustrates the hydrogen atom diffusion process. Both samples demonstrated good activation performance.

Figure 5 shows that the discharge capacity of the nanoelectrodes increases with the number of cycles. The maximum discharge capacities are 1320 mAh/gr and 1210 mAh/gr for S1 and S2 after 12 cycles, respectively. The combination of Co with the functionalized MWCNTs resulted in greater activation than S2, which combines Fe with functionalized MWCNTs. After surface treatment, the MWCNTs provide active sites to attract hydrogen ions. On the other hand, Co has lower electrical resistivity and greater stability than Fe [25], allowing it to exhibit better reduction activity. Therefore, the S1 nanoelectrode has a greater hydrogen discharge capacity than the S2 nanoelectrode.

Conclusion

In this study, a dropwise method was used to cover a Co(Fe)/Cu electrode with purified MWCNTs. These nanoelectrodes were subsequently utilized as active materials for investigating their hydrogen storage capacity. The chronopotentiometry method was employed to determine the discharge process. The results showed that the Co/MWCNT nanoelectrode, with a discharge capacity of 1320 mAh/grdoe, was more efficient than the Fe/MWCNT nanoelectrode due to its greater reduction activity. Therefore, these nanoelectrodes have potential applications in hydrogen storage.

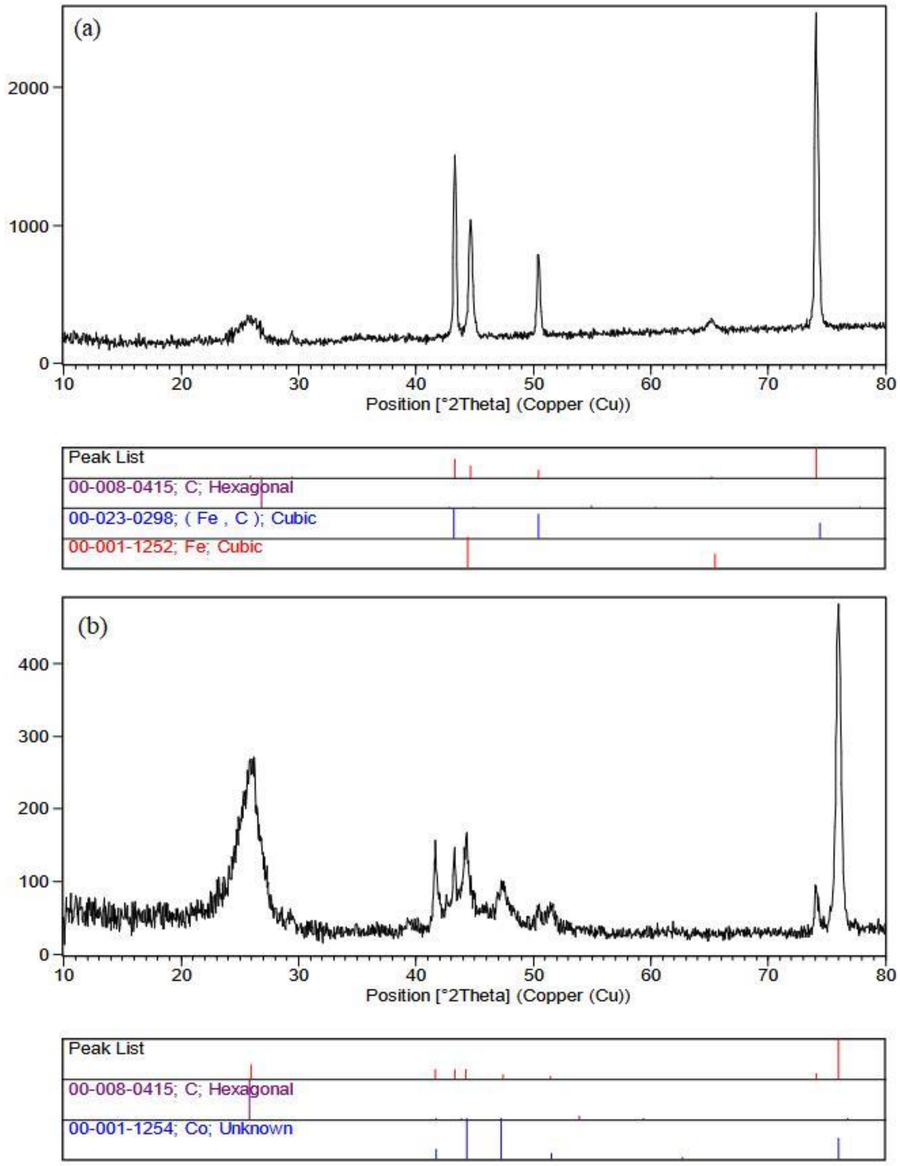

Figure 1. XRD analysis of the (a), Fe/MWCNT nanoelectrode, and (b) Co/MWCNT nanoelectrode.

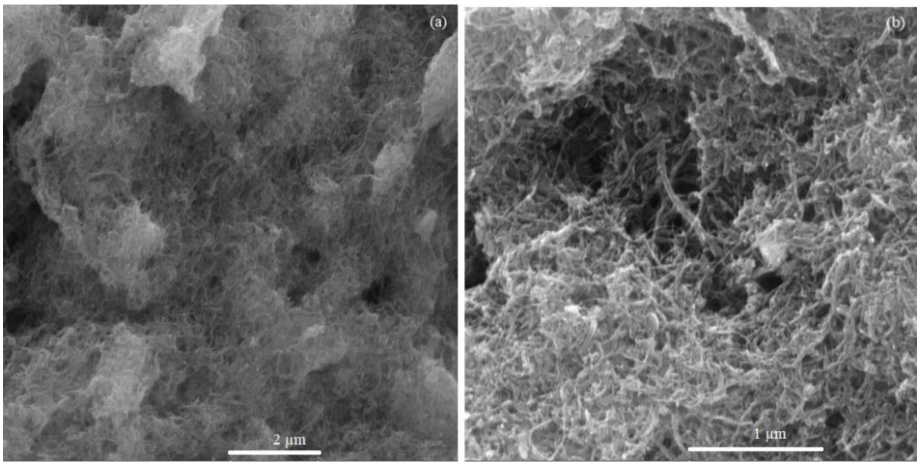

Figure 2. SEM images of the (a), Fe/MWCNT nanoelectrode, and (b) Co/MWCNT nanoelectrode.

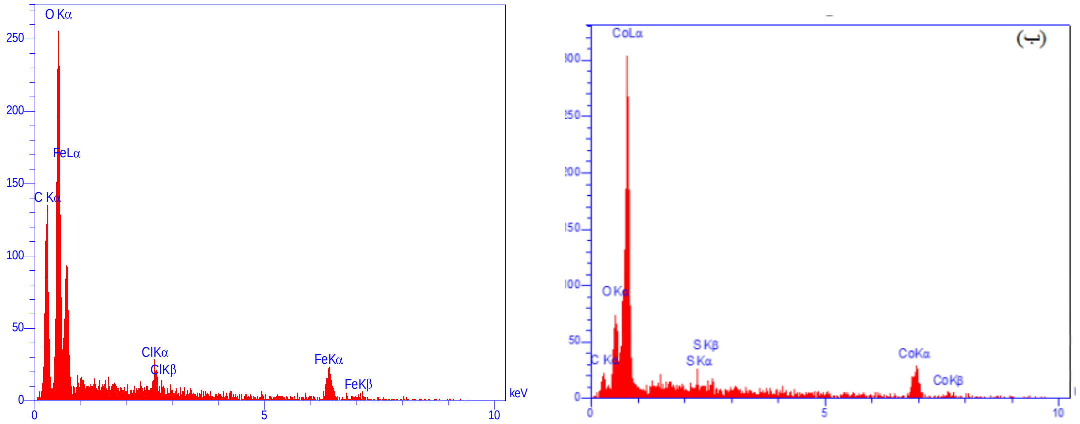

Figure 3. EDX spectrum of the (a), Fe/MWCNT, and (b) Co/MWCNT nanoelectrodes

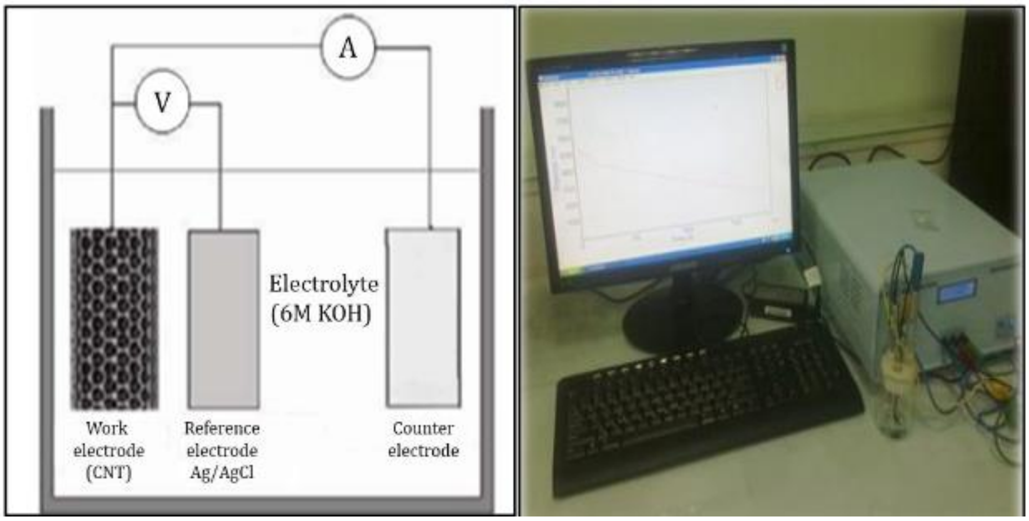

Figure 4. The setup of this work and a schematic image which indicates the Chronopotentiometry method.

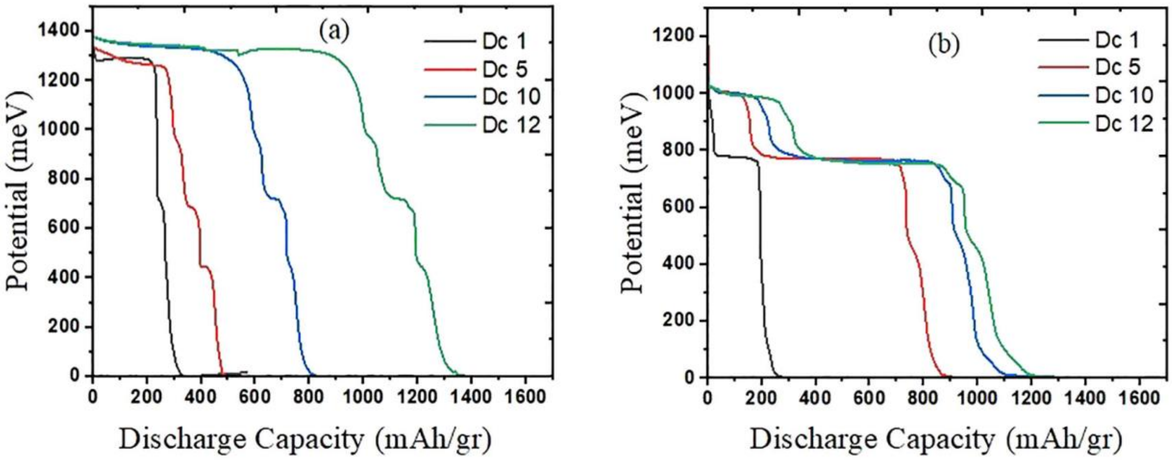

Figure 5. Hydrogen discharge capacity (DC) curves of the (a) Co/MWCNT nanoelectrodes, and (b) Fe/MWCNT nanoelectrode.

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