Hydrogen storage in carbon nanotubes with Ni nanoparticles by electrochemical

ABSTRACT

In this paper, the electrochemical hydrogen storage in nanocomposite materials was studied. Multi-Walled Carbon Nanotubes (MWCNTs) electrode was prepared by mixing with special composite. The optimum ratio of MWCNTs was estimated 30-70% (w/w) in the composite material. MWCNTs were synthesized by Chemical vapor deposition (CVD). The nanocomposite was homogenized by microwave. Cyclic voltammetry (CV) was applied to study the behavior of electrode. Ni nanoparticles were electrodeposited on working electrodes via dual-pulse method. Voltammograms indicated that, Ni nanoparticles have electrocatalytic effect on hydrogen storage capacity.

Keywords: Hydrogen; Nanocomposite; Ni nanoparticles.

INTRODUCTION

Hydrogen is the renewable source of energy, so it has been categorized as green source [1-2]. In future, we would have many environmental problems due to utilizing Fossil fuels [3]. Hydrogen, unlike fossil fuels, is a clean energy source, which does not release harmful gases into the environment. However up to now, scientists have not accessed to high efficient and applicable method for hydrogen storage. Regarding the department of energy (DOE) [4], it is essential to store up to 6.5 wt% of hydrogen in system to be utilized as hydrogen resources in fuel cells. Methods, which are used to store hydrogen, such as liquefaction or hydrogen compression, not only waste a lot of energy, but also have safety problems. Chemical or physically combined hydrogen storage in materials has been studied by many researchers. In recent years, metal hydrides attract much attention. Some compounds like LaNi5, ZrV2, FeTi, and Mg2Ni make a bond with hydrogen but, releasing the stored hydrogen require high temperature [5]. Since carbon nanotubes (CNTs) were discovered by Iigima, they attract much attention for use in various scientific fields [6].
Carbon nanotubes have been investigated intensively for the usage as hydrogen storage material since 1997 [7-8]. Micro porous and ultra-micro porous carbonaceous materials are appropriate to reversible gas storage. Due to micro porous structure of CNTs, they are convenient candidate for safe hydrogen storage [9-10]. Hydrogen storage capacity would be increased via doping nanoparticles such as Ti, Li, Ni, Fe and V [11-12]. Lizheh gao et al. [13] showed that, hydrogen storage is not efficient in pristine CNTs. However, the hydrogen storage capacity of MWCNTs will be increased via oxidation and loading nanoparticles of pd-Ni. Chun-chen yang et al. obtained the electrochemical discharge capacity of 1404 mAhg\(^{-1}\) for Ni-doped single-walled carbon nanotubes (SWCNTs), correspond in 5.27 wt% for hydrogen storage [14]. A. Reyhani et al. [15] studied the electrochemical hydrogen storage on raw, oxidized, purified and Fe-doped MWCNTs. They realized that, Fe-doped MWCNTs were produced with high capacities.

In this study, for the first time, electrodes were prepared by MWCNTs and special composites. MWCNTs were synthesized by CVD method. Cyclic voltammetry was applied to study the behavior of prepared electrodes. Afterwards, Ni nanoparticles were electrodeposited on electrodes to study the behavior of Ni-CNTs electrodes.

**EXPERIMENTAL**

**Electrode preparation**

Fe-doped MWCNTs and special composite were used to fabricate working electrodes. MWCNTs and composite were mixed and acetone was added as solvent. As a first step, the conductivity of the prepared nanocomposite was examined to evaluate the optimized percentage MWCNTs and composite. The optimized percentage of the mix were chosen to 30-70 wt. % Then microwave was irradiated to homogenize the nanocomposite.

**Electrodeposition of Ni and Pt nanoparticles**

In this stage the effects of Ni nanoparticles were studied. First of all, a solution of Ni (NO\(_3\))\(_2\).6H\(_2\)O with concentration of 1.0x10\(^{-3}\) M was prepared. The electrodeposition was done in a three-electrode system using Ni(NO\(_3\))\(_2\).6H\(_2\)O solution as electrolyte. Cyclic voltammetry measurements in a potential range of -0.4 to -1.6 were applied to evaluate the reduction potential of Ni salt. Also, Ni nanoparticles were electrodeposited on electrode via double-pulse technique. For this purpose, the potential of -0.9 V and -0.85 V was applied to electrode for 5 and 10 s, respectively.

**Electrochemical measurements**

Hydrogen uptake measurements of nanocomposites were studied in three-electrode system, in which NaOH 6.0 M was used as electrolyte. A Pt electrode and Ag/AgCl (3.0 M) electrodes were applied as counter and reference electrodes, respectively. Potentiostat-Galvanostat, µAutolab type III set was used. The experiments were done in ambient pressure and temperature. CV of prepared electrodes were studied in a potential range of -1.6 to +0.6 V with scan rates of 20, 50, 100 and 150 mV s\(^{-1}\), for activation as well as conversoin hydphobicity of the composite to hydrophilic one, the nanocomposite was kept in NaOH (6.0 M) for ~8 h before obtaining the desired baseline.

**RESULTS AND DISCUSSION**

**Hydrogen storage**

CV was used to study the electrochemical behavior of prepared electrodes. To investigate the oxidation and reduction peaks, potential was scanned from -1.6 to 0.6 V (vs. Ag/AgCl), at the scan rates of 20, 50, 100 and 150 mV s\(^{-1}\). Figure 1 shows the voltammograms at different scan rates. Regarding to Figure 1, the continuous CVs are overlapped on each other, concluding that, the process of this phenomenon is governed by diffusion process. Figure 1, demonstrates a linear relationship between the square root of scan rate (\(\gamma^{1/2}\)) and oxidation/reduction peak currents. Also, the highest current was expected at 200 mV s\(^{-1}\), however it should be noticed that high scan rates resulted in increasing oxidation/reduction rates, but, on the other hand, the thickness of electrical double layer increased, and these two phenomenon worked against. Hence coordination should be existed between scan rate and the thickness of electrical double.
Fig. 1. Voltammograms of Fe-doped MWCNTs at scan rates of (a) 20, (b) 50, (c) 100 and (d) 200 mVs$^{-1}$.

As clearly observed according to the voltammogram shown in Figure 1, reduction peaks positioned at -0.7 (a) and -0.88 V (b) are related to the reduction of dissolved O$_2$ into HO$_2^-$ and OH$^-$, respectively. As also demonstrated in Figure 1, hydrogen adsorption and desorption occurred at around -1.4 (c) and -0.23 V (d), respectively.

**The effect of Ni nanoparticles**

The cyclic voltammetry was utilized to evaluate the reduction of Ni salt on electrodes. The potential applied in the range of -0.4 to -1.6 V (vs. Ag/AgCl). Figure 2 demonstrates the reduction of Ni salt carried out in -0.75 V (vs. Ag/AgCl). Afterwards, the behavior of this electrode was studied through cyclic voltammetry measurements.

Figure 3 shows the effect of Ni nanoparticles on working electrode. As shown (Figure 3), the behavior of electrode changed and adsorption and desorption current intensities improve.

It demonstrates that the reduction potential related to the adsorption of hydrogen on the Ni-electrodeposited MWCNTs was significantly shifted from (~1.42 V) to the less negative potentials (-1.36 V). So, the potential range becomes more restricted. Also, the adsorption peak becomes sharper. Hence, Ni nanoparticles act as catalyst in this method.
Then, double-pulse technique was used to electrodeposit Ni nanoparticles on electrode. Cyclic voltammetry measurements were utilized to study the effect of Ni nanoparticles.

As shown (Figure 4) significant changes were observed in the adsorption and desorption peak current intensities during the electrodeposition of either Ni nanoparticles using each double-pulse technique.

CONCLUSION

In this study, electrochemical hydrogen storage of special nanocomposite was investigated. Voltammograms at different scan rates reveal that there is a proportional relation between current intensity and scan rate. Also, the effect of Ni nanoparticles was studied. The voltammograms show that Ni nanoparticles acts as active sites and improve the hydrogen storage capacity. Also, the results show that at different cycles, the hydrogen storage process is followed by diffusion.

REFERENCES


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