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Electrochemical hydrogen storage of Pt and Ni nanoparticles-electrodeposited multi-walled carbon nanotube/micro-hybrid composite

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ABSTRACT

Cyclic voltammetric (CV) hydrogen storage of multi-walled carbon nanotube (MWCNT)/micro-hybrid composites is studied. For this purpose, a three-electrode system is utilized using a Pt disk as counter, Ag/AgCl (3.0 M) as reference and MWCNT/micro-hybrid composite as working electrodes. Optimum percentage of MWCNTs in the composite matrix is suggested to 50% (w/w). Solution of NaOH (6.0 M) is also selected as electrolyte. Hydrogen adsorption/desorption behavior of composite is investigated based on CV measurements in the range of −1.60 to +0.50 V (vs. Ag/AgCl). Chrono-amperometery is applied to estimate active surface area of the composite (0.145 $m^2 g^{-1}$) and diffusion coefficient (3.41×10^{-11} $m^2 s^{-1}$) of adsorbed hydrogen. According to the results, the active surface area and also the diffusion coefficient of H_2 are significantly promoted when thermally activation of the CNT-based composite by O_2, or assisting to ultraviolet (UV) radiation and/or microwave irradiator. In this fstudy, the effect of nanoparticles such as Ni and Pt is also investigated via electrodeposition of Ni(II) and $PtCl_4^{2-}$ on the CNT-based composite using single- and double-pulse methods. According to the voltammograms, significant enhancements are observed in the reduction peak currents of hydrogen, when decorating Ni or Pt nanoparticles. Ultimately, hydrogen capacity of fabricated composite is evaluated to 4.62 wt.%, after charging the CNT-based composite for a certain time (~1 h).

1. Introduction

As hydrogen is a renewable source of energy, this gas has been categorized as green source [1,2]. In future, human would have much more environmental problems due to utilizing the fossil fuels [3]. Also, using green source of energies, such as wind, solar and geothermal energies, waste and pollution would be declined [4]. Hydrogen, unlike fossil fuels, is clean energy sources, which does not release harmful gases into the environment. However, till now, scientists have not accessed to a high efficient and applicable method for hydrogen storage. Regarding to department of energy (DOE) [5], it is essential to store up to 6.5 wt.% of hydrogen in systems to be utilized as hydrogen resources in fuel cells. Also, due to the expansion limit of hydrogen, the storage capacity should be achieved at ambient pressure and temperature, followed by releasing hydrogen at environmental circumstances. Reversibility and stability of stored hydrogen significantly have been concerned the scientist's attention during recent years [6,7]. Methods, which are usually used to store hydrogen, such as liquefaction or hydrogen compression, not only, waste a lot of energy, but also, have safety problems [5]. Various materials such as metal hydrides or carbon nanostructures are usually used for physicochemical hydrogen storage and evolution [8–10].

Metal hydrides, due to possessing high storage density and light weight, can be considered as appropriate candidate to store hydrogen. However, due to the slow hydrogen sorption kinetics, these alloys require high temperature for hydrogen adsorption/desorption [8]. Microporous and ultramicroporous carbonaceous materials are also considered as appropriate absorbers for reversible gas storage [9]. Among carbon allotropes, carbon nanotubes (CNTs), due to their microporous structure, are convenient candidate for safety hydrogen storage [10,11].

Hydrogen storage capacity would be promoted via doping metal nanoparticles such as Ti, Li, Ni, Fe or V [12–16]. Gao et al. showed that, hydrogen storage is not efficient in pristine CNTs [17]. However hydrogen storage capacity of multi-walled carbon nanotubes (MWCNTs) would be increased through addition of pd–Ni nanoparticles [17]. Yang et al. obtained the electrochemical discharge capacity of 1404 mA h g^{-1} for Ni-doped single-walled carbon nanotubes (SWCNTs) [14]. Reyhani et al. studied the electrochemical hydrogen storage on raw, oxidized, purified and Fe-doped MWCNTs [18]. They realized that, Fe-doped MWCNTs

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produced the highest capacities [18]. They also showed that, acid treatment by HF provides the highest surface area, compared to those treated with HNO_3, HCl or H_2SO_4 [19]. However CNTs have unique properties such as high active surface area and high defects [10,11,20], these nanomaterials have disadvantages such as low capacity for hydrogen storage, low mechanical stability or irreversibility of hydrogen. To solve these problems, in this work, hydrogen storage behavior of a new kind of carbon paste electrode, fabricated by Ni or Pt nanoparticles-decorated MWCNT/micro-hybrid composite is investigated in detail.

2. Experimental

2.1. Reagents and materials

MWCNTs and micro-hybrid composite (Vericom Co. Korea) were used to fabricate the working electrode. MWCNTs were synthesized by chemical vapor deposition (CVD) method. NaOH (6.0 M, Merck, Darmstadt, Germany) was used as electrolyte. Highly pure acetone (Merck, Darmstadt, Germany), was utilized to prepare a homogeneous composite. $Ni(NO_3)_2{\cdot}6H_2O$ (Merck, Darmstadt, Germany, 1.0 mM) and K_2PtCl_6 (Merck, Darmstadt, Germany, 0.01 M) solutions were prepared as precursor of Ni and Pt nanoparticles, respectively. Solution of 1.0 mM $K_4Fe(CN)_6$ was also prepared as detection probe.

2.2. Composite preparation

MWCNTs and a micro-hybrid resin were used to fabricate the composite. For this purpose, electrical resistance of the composites with different percentages of MWCNTs was examined. The optimum percentage of MWCNTs in the mixed material was chosen to 50 wt.%. For this purpose, ~0.02 g of MWCNTs was mixed with 0.02 g of micro-hybrid resin, followed by addition of ~10 ml of acetone (Merck, Darmstadt, Germany) as homogenizer. Microwave (Samsung, Power = 1200 W) radiation and ultraviolet (UV, Power = 600 W, λ = 360 nm) were also applied to improve the surface activity of composite. To prepare working electrode, the composite material was packed into a glass tubing (i.d. 2.0 mm). A copper wire was then used to provide the electrical connection. According to the TEM image, the size of MWCNTs was estimated to ~70 nm.

2.3. Activation of MWCNT-based composite

Due to the high hydrophobicity of the carbon nanostructures, CNT-based electrode should be activated. In this study, MWCNTs were activated thermally via purging oxygen to the CVD instrumentation system [21,22], or via irradiation with UV or microwave. Before, using the composite as working electrode, its hydrophilicity was also promoted via putting the CNT-based composite in NaOH solution (6.0 M) for ~12 h.

2.4. Electrochemical measurements

Three-electrode system was used to study the electrochemical hydrogen storage behavior of the composite using NaOH (6.0 M) as electrolyte. Pt disk and Ag/AgCl (3.0 M) were applied as counter and reference electrodes, respectively. The prepared composite was utilized as working electrode. The experiments were achieved in ambient pressure and temperature. CV measurements were investigated using Potentiostat–Galvanostat, μAutolab type III set in the potential range of −1.60 to +0.50 V (vs. Ag/AgCl) in different scan rates including 20, 50, 100 and 150 mV s^{-1}. The capacity of electrode was measured by galvanostatic charge/discharge after charging the composite for a certain time (~1 h). Chronoamperometry was also used to evaluate the active surface area and diffusion coefficient of decorated MWCNT/micro-hybrid composite using $K_4Fe(CN)_6$ as detection probe by "Cotrell" equation [20].

2.5. Electrodeposition of Ni and Pt nanoparticles

To study the effects of Ni and Pt nanoparticles on hydrogen adsorption/desorption, electrodeposition was done in the three-electrode system using either $Ni(NO_3)_2{\cdot}6H_2O$ (1.0 mM), or K_2PtCl_6 (0.01 M), solution as electrolyte. CV measurements were used to evaluate the reduction potential of each Ni(II) or $PtCl_4^{2-}$ salt. Single- and double-pulse techniques were also utilized for electrodeposition of Ni and Pt nanoparticles.

To electrodeposit Ni and Pt nanoparticles via single-pulse method, a certain direct current (DC) potentials equal to −0.90 V and −0.85 V, were applied to the CNT-based composite for 5.0 and 10.0 s, respectively. Whereas, to electrodeposit Ni and Pt nanoparticles via double-pulse process, negative potentials equivalent to −0.80 V and −0.25 V were initially applied to the working electrode for 5.0 s to form nuclei of each Ni and Pt nanoparticle, respectively. Then, to growth Ni and Pt nanoparticles, less negative potentials of −0.75 V and −0.20 V were applied to the working electrode for 10.0 s, respectively.

3. Results and discussion

3.1. Selection of carbon nanostructure

Due to the presence of plenty of edge planes in the MWCNT matrix, these nanostructures are usually adopted for electrochemical process. This property, in additional to the microporous morphology and high defects of MWCNTs, provide active sites for charge transfer process, particularly when activating CNTs via purging O_2 or treatment by UV and/or microwave. Also, keeping the composite in NaOH (6.0 M), for ~12 h promotes the hydrophilicity of the composite.

3.2. Ratio of composite/CNT

The electrical conductivity of CNT-based composite was examined in different weight ratio of MWCNTs/micro-hybrid resin. Homogeneous paste composite with minimum standard deviation was observed at 40–70 wt.% of MWCNT/micro-hybrid. Consequently, ratio of 50 wt.% was selected as optimum ratio. Peaks positioned at ~25° and 45° indicate the presence of graphite plane [23]. Significant differences, at 2θ = 23° and 42°, reveal the formation of new phase during activation of MWCNT-based composite.

3.3. Effect of electrolyte

As less negative potential is required for hydrogen evolution during the reduction reaction, alkaline solution is commonly utilized [18,24]. In this work, NaOH solution was selected as electrolyte. To have the highest efficiency for hydrogen evolution on the composite, several concentrations of NaOH extending from 0.5 M to 7.0 M were studied. The furthermost efficiency was evaluated at concentration to ~6.0 M. At concentrations superior to ~6.5 M, adsorption activity of the composite is somewhat degraded (~5%) possibly, owing to the salting-out effect of the electrolyte [25]. Consequently, 6.0 M-NaOH solution was considered as optimum concentration for hydrogen evolution.