



The effect of various acids treatment on the purification and electrochemical hydrogen storage of multi-walled carbon nanotubes

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ABSTRACT

The effects of HCl, HNO₃, H₂SO₄ and HF acids on the purification and the electrochemical hydrogen storage of multi-walled carbon nanotubes (MWCNTs) were studied. The MWCNTs were synthesized on Fe–Ni catalyst by thermal chemical vapor deposition method. The X-ray diffraction and thermal gravimetric analysis results indicated that the MWCNTs purified by HF acid had the highest impurities as compared with the other acids. The N₂ adsorption results at 77 K indicated that all the samples were mainly mesoporous and the purified MWCNTs by HF acid had the highest surface area as compared with the other acids. The hydrogen storage capacities of the purified MWCNTs by the following acids were in ascending order as: H₂SO₄, HCl, HNO₃ and HF. It was found that the 1–2 nm micropores in the MWCNTs are very important for hydrogen storage. Further, the presences of catalyst and defective sites in MWCNTs influence the hydrogen storage capacity.

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1. Introduction

Since the discovery of multi-walled carbon nanotubes (MWCNTs) by Iijima [1] and then synthesis of single-walled carbon nanotubes (SWCNTs) by Iijima and Lchihashi [2] as well as Bethune et al. [3], carbon nanotubes (CNTs) became one of the promising nanomaterials leading to special applications such as energy storage, display, optoelectronics and bio-medicine, due to their perfect structures exhibiting unique electronic, physical and mechanical properties [4]. Various methods have been used for the growth of carbon nanotubes, including SWCNTs and MWCNTs. Thermal chemical vapor deposition (TCVD) method has many advantages over the other methods due to its simplicity and low cost. In TCVD method, the catalyst materials, usually transition metals such as Ni, Co, Fe or their binary alloys, are used for the growth of CNTs [5,6].

Nowadays, hydrogen is recognized as an ideal fuel for energy converters because of the high efficiency and its role in the reduction of air pollution [7]. However, due to the existence of major scientific challenges, it has not been used in great extent up to now. In addition, hydrogen storage with a safe, effective and cheap system is the main problem of its practical usage [8–10]. Many attempts have been done for hydrogen storage so far, but none of

them have completely satisfied the determined standard by the US Department of Energy (DOE) [8].

Since the report of Dillon et al. on a possible 5–10% hydrogen storage capacity for SWCNTs, CNTs have attracted much attention in new porous materials for safer hydrogen storage [11]. Hydrogen storage by CNTs may be accomplished through physical adsorption or electrochemically from aqueous solutions. It has been widely reported that growth method [12], synthesis condition [13], purification [14–19] and structure [20] of CNTs have a strong effect on hydrogen storage capacity. Many studies have revealed that micropores (<2 nm) or even smaller pores are essential for hydrogen storage [21]. Lombardi et al. [22] measured the hydrogen storage capacities for MWCNTs as produced and after nitric acid treatment. They reported that nitric acid treatment improved hydrogen uptake. Yoo et al. [23] also reported that the defective sites on the MWCNTs are adsorption sites for atomic hydrogen.

In this paper, the MWCNTs were synthesized in large quantity by TCVD method. The effects of HCl, HNO₃, H₂SO₄ and HF acids on the purification and electrochemical hydrogen storage of MWCNTs were also studied. The scanning electron microscopy (SEM), X-ray diffraction (XRD), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), Brunauer–Emmett–Teller (BET), Barret–Joyner–Halenda (BJH) and Raman spectroscopy techniques were used to evaluate the structure, graphitization, quality and adsorption characteristics of the purified MWCNTs by HCl, HNO₃,

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H₂SO₄ and HF acids. Cyclic voltammetry and chronopotentiometry were applied to determine the electrochemical measurement of the samples.

2. Experimental

2.1. Catalyst preparation

Bimetallic catalysts of Fe and Ni supported by MgO (with the proportion of 2:2:6) were prepared using a wet chemical impregnation method. In a typical synthetic procedure, 1 g of MgO powder (99.9%-merck) dispersed in 20 ml of distilled water and the obtained suspension was sonicated for 30 min in order to get a homogeneous suspension. Then, appropriate amounts of the aqueous solutions of metal nitrates (Fe (NO₃)₃·9H₂O and Ni (NO₃)₂·6H₂O) were added to the MgO suspension and the mixture was stirred for 30 min. The prepared impregnate was dried in an oven at 150 °C for 24 h in air. After drying the mixture, it was ground to fine powder.

2.2. MWCNTs growth

After preparation of the catalyst, the sample was loaded into a quartz tubular furnace at the atmospheric pressure. An amount of the calcined catalyst (0.5 g) was placed in a ceramic boat (40 mm × 130 mm), and then settled into the central part of the quartz tube. The furnace was heated from the room temperature to 700 °C, in Ar gas flow (80 sccm) for 40 min when the temperature reached to 700 °C, a mixture of Ar (20 sccm) and H₂ (60 sccm) was fed into the furnace. The furnace was heated further to 900 °C in 10 min and at 900 °C, the ramping of temperature was stopped. After the temperature stabilized at 900 °C, the mixture flow was stopped and a flow of NH₃ (80 sccm) was introduced at the same temperature for 40 min to reduce the catalyst inside the quartz tube. Then, the furnace was further heated up to 940 °C in 10 min under H₂ flow at 80 sccm. When the temperature stabilized at 940 °C, high purity CH₄ gas was introduced into the tubular furnace at a flow rate of 80 sccm for 40 min to induce the catalytic pyrolysis of CH₄ to form CNTs. After the growth of CNTs, the furnace was cooled to the room temperature under Ar gas flow.

2.3. Purification of the grown CNTs

Purification of MWCNTs was performed by four various acids in order to determine the effect of purification procedure for hydrogen storage. First, raw MWCNTs were placed in the boat, and calcined in the furnace at 450 °C for 60 min in O₂ at ambient pressure, and then cooled down to room temperature. The same amounts of MWCNTs were separately immersed in 3 M solutions of different acids of HNO₃, H₂SO₄, HCl and HF for 24 h at room temperature. Then, the MWCNTs were washed out several times with deionized water until the pH value of the solution became neutral. The samples were then dried at 150 °C for 24 h in ambient.

2.4. Sample characterization

Characterization of the samples was carried out by the following techniques: Philips XL30 SEM was used for determination of the MWCNTs' morphology and diameter. TGA and DSC techniques were employed to investigate the MWCNTs' yield and graphitization using a Rometric simultaneous thermal analysis (STA). The samples were heated from 30 to 850 °C at a rate of 10 C min⁻¹ in ambient air. Raman spectroscopy HR-800 Jobin-Yvon was utilized to determine the quality of the purified MWCNTs. The Raman spectra were recorded from 200 to 2000 cm⁻¹.

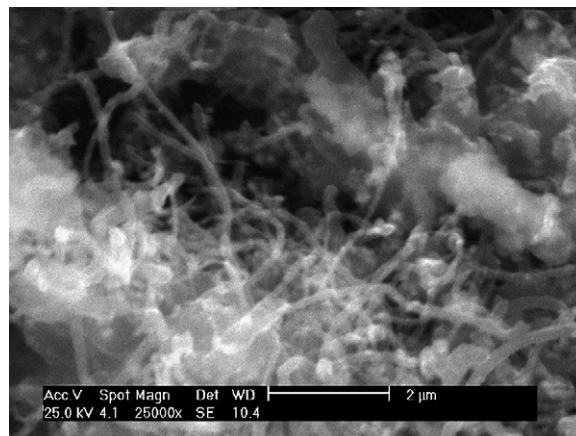


Fig. 1. SEM micrographs of the raw MWCNTs.

Graphitization and structure of the MWCNTs, structure of the impurities such as Fe–Ni catalyst and MgO were characterized by XRD (Cu K α X-ray radiation source) with 2θ from 20 to 80°. The scanning speed and step interval were 1° min⁻¹ and 0.02°, respectively. A high-performance volumetric physisorption apparatus at 77 K (BET) was used to determine the CNTs' surface area. Pore size distribution of the MWCNTs was also obtained by BJH equation using the adsorption isotherm.

2.5. Preparation of electrodes and electrochemical measurements

The purified MWCNTs obtained by different acids were used to fabricate the electrodes. Prior to formation of the electrodes for electrochemical tests, 2 mg of CNTs was added into a solution of nafion (0.1 ml) and DI water (3 ml), and the obtained solution was sonicated for 30 min. A stainless steel plate was used as cathode matrix (20 mm × 40 mm × 1 mm). After burnishing, it was corroded in a HF solution (30%) for 20 min. The electrodes were prepared by dropping the sonicated solution of MWCNTs on the porous stainless steel plate. Then the electrodes were dried in an oven at 100 °C for 2 h. Electrochemical hydrogen storage was studied with a three-electrode system (Autolab 302) at ambient temperature by using a 6 M solution of NaOH as the electrolyte.

A Ni wire was used as the counter electrode and an Ag/AgCl electrode as the reference electrode. Cyclic voltammetry (CV) measurements of the prepared CNTs electrodes were done in a potential range of –1.5 to 0.5 V with six scanning rates of 5, 10, 20, 30, 50 and 100 mV s⁻¹. The experiments on charging/discharging were carried out by charging the electrodes for 30 min in the constant current of 5 mA and discharging them under the similar conditions.

3. Results and discussion

3.1. Characterization of MWCNTs

A SEM micrograph of as-grown sample of MWCNTs is shown in Fig. 1. It is observed that the raw materials consisted of MWCNTs and impurities such as catalyst particles. The diameter distribution was in the range of 50–100 nm.

The Raman spectra of the raw and purified MWCNTs by HCl, HNO₃, H₂SO₄ and HF acids are shown in Fig. 2. The Raman bands appearing in 1500–1605 and 1250–1450 cm⁻¹ of the spectrum are known as G and D, which can be assigned to the C–C vibration of graphite and disordered structure (such as intrinsic defects in the CNTs or amorphous carbons located on the CNTs bands), respectively. It is known that the intensity ratio of the G and D peaks

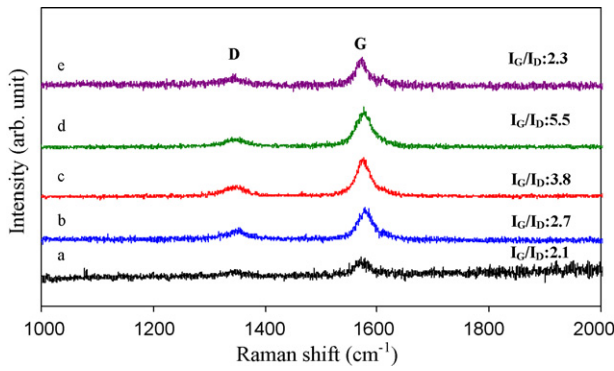


Fig. 2. Raman spectra of the (a) as-grown CNTs and the purified MWCNTs by: (b) HCl, (c) HNO₃, (d) H₂SO₄ and (e) HF acids.

(I_G/I_D) is used as a rough measure of sample quality [24,25]. The results of Raman spectra indicated that the I_G/I_D ratios of the raw and purified CNTs by HCl, HNO₃, H₂SO₄ and HF acids are about 2.1, 2.7, 3.8, 5.5 and 2.3, respectively.

TGA and DSC curves derived from STA were used to determine the percentage of all the carbon species (the amorphous carbon and CNTs) and graphitization of CNTs. The percentages of the amorphous carbon and CNTs were obtained according to weight loss at 300–400 °C and 500–800 °C, respectively. TGA and DSC results of the raw and purified MWCNTs using different acids are shown in Table 1. In terms of TG analysis, Table 1 shows the yield of CNTs for the raw and purified MWCNTs using HCl, H₂SO₄, HNO₃ and HF acids as 48.5, 92.6, 87.1, 82.3 and 51.2%, respectively.

Lack of weight loss in the raw MWCNTs from 300 to 400 °C indicates that no amorphous carbon existed in the raw MWCNTs. But, as Table 1 shows, after purification treatment, we observed the destruction of MWCNTs in form of amorphous or non-crystalline carbon. The percentages of the amorphous carbon in the purified MWCNTs by using HCl, HF, HNO₃ and H₂SO₄ acids were determined to be 1.1, 0.7, 0.2 and 0.1%, respectively. It is considerable that the MWCNTs purified by HCl and HF acids contained higher amorphous carbons than those purified by H₂SO₄ and HNO₃ acids. This destruction in the MWCNTs was confirmed by Raman spectra. This result may be explained by the corrosive effect of HCl and HF acids on the outer walls of the CNTs that produced amorphous carbons. Also, the difference between the onset and offset burning temperatures of the CNTs in TGA indicated that the purified CNTs by HCl and HF acids contained carbon structures with less structural diversity in comparison with those purified by H₂SO₄ and HNO₃ acids.

In addition, the DSC results (Table 1) illustrated that the inflection temperatures of the purified MWCNTs by the following acids were in descending order H₂SO₄, HCl, HNO₃ and HF acids. The increasing of the inflection temperature is indicative of the improvement in graphitization properties of the MWCNTs [26].

The XRD results of the purified MWCNTs by HCl, HNO₃, H₂SO₄ and HF acids are shown in Fig. 3. The peak appeared at around $2\theta = 26.3^\circ$ is characteristic of MWCNTs, the peaks at $2\theta = 42.9^\circ$ and 62.35° are characteristic of MgO, the peaks at $2\theta = 40.5^\circ$ and 53.7°

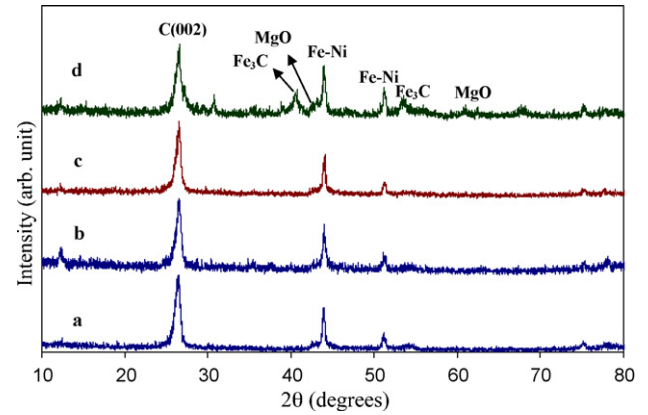


Fig. 3. XRD results of the purified MWCNTs by: (a) HCl, (b) HNO₃, (c) H₂SO₄ and (d) HF acids.

indicate Fe₃C and the peaks at $2\theta = 43.9^\circ$ and 51.05° are indicative of Fe–Ni alloy. The investigation of XRD results (Fig. 3) indicated that the purified MWCNTs by HF acid had the highest impurities (such as MgO, Fe₃C and Fe–Ni) as compared with other acids. These results were confirmed by TGA. Also, the XRD results showed that the impurity of the purified MWCNTs by HCl, HNO₃ and H₂SO₄ acids was only Fe–Ni.

The N₂ adsorption at 77 K is known as a method to determine the pore size distribution, pore volumes and specific surface area of porous materials. Fig. 4 depicts N₂ adsorption isotherm of the purified MWCNTs by HCl, HNO₃, H₂SO₄ and HF acids. The isotherms obviously indicate the adsorption hysteresis behavior in the P/P_0 range from 0.4 to 0.99 (Fig. 4). So, all the samples were mainly mesoporous. Fig. 5 shows the pore structures (BJH) of the purified MWCNT by HCl, HNO₃, H₂SO₄ and HF acids. The major peaks

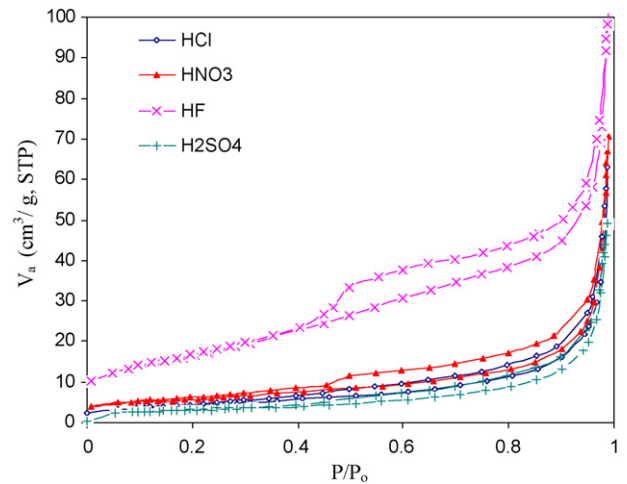


Fig. 4. N₂ adsorption and desorption isotherms of the purified MWCNTs by HCl, HNO₃, H₂SO₄ and HF acids.

Table 1
TGA and DSC results of the purified MWCNTs by HCl, HNO₃, H₂SO₄ and HF acids

MWCNTs samples	Onset temperature (°C)	Inflection temperature (°C)	Offset temperature (°C)	Amorphous carbon (%)	Weight loss (%) at 500–800 °C (CNTs yield in the sample)
Raw	508	648	698	0	48.5
Purified by HCl	511	664	719	1.1	92.6
Purified by HNO ₃	503	661	715	0.2	82.3
Purified by H ₂ SO ₄	556	700	751	0.1	87.1
Purified by HF	540	644	713	0.7	51.2

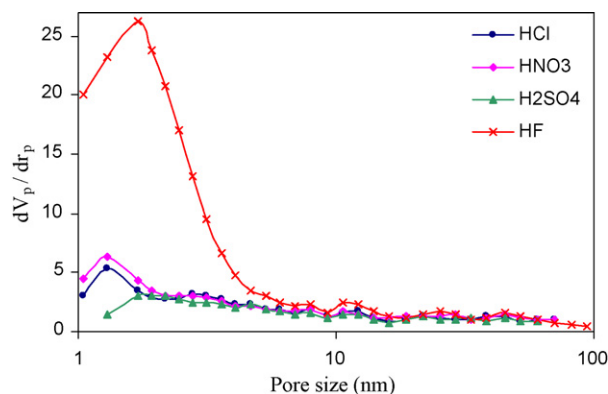


Fig. 5. Pore size distribution of the purified MWCNTs by HCl, HNO₃, H₂SO₄ and HF acids.

of the purified MWCNTs by HCl, HNO₃, H₂SO₄ and HF acids were about 1.29, 1.3, 1.71 and 1.7 nm, respectively. The surface characterizations of the purified MWCNTs by HCl, HNO₃, H₂SO₄ and HF acids obtained from the N₂ adsorption isotherm are summarized in Table 2. Accordingly, the purified MWCNTs by HF acid have the highest surface area in comparison with the other acids. This fact may be explained by the increase in volume of the micropores (1–2 nm) of the purified MWCNTs after HF acid treatment.

3.2. Hydrogen storage

The cyclic voltammetry behavior of the purified MWCNTs by HCl, HNO₃, H₂SO₄ and HF acids in 6 M NaOH solutions was studied

Table 2
Surface characteristics of the purified MWCNTs by HCl, HNO₃, H₂SO₄ and HF acids from nitrogen physisorption at 77 K

Purified MWCNTs by	BET surface area (m ² g ⁻¹)	Peak pore volume (cm ³ g ⁻¹)	Peak pore sizes (nm)
HCl	13.58	0.095	1.29
HNO ₃	19.86	0.1	1.31
H ₂ SO ₄	10.56	0.075	2.17
HF	57.59	0.15	1.72

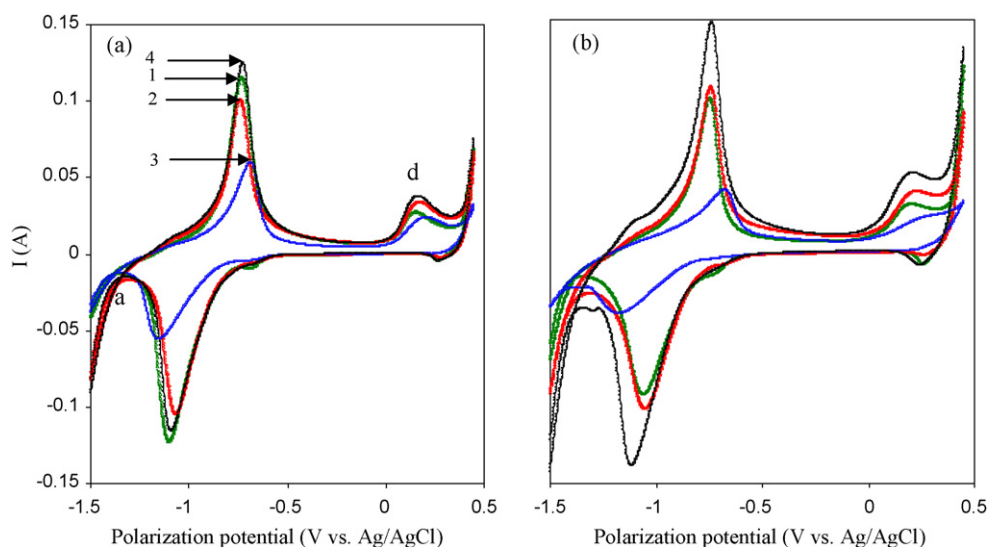


Fig. 6. Cyclic voltammetry of the electrodes assembled with the purified MWCNTs by (1) HCl, (2) HNO₃, (3) H₂SO₄ and (4) HF acids at various sweep rates (a) 20 and (b) 50 mV s⁻¹.

Table 3
Hydrogen storage data of the purified MWCNTs by HCl, HNO₃, H₂SO₄ and HF acids in the electrochemical method

Purified MWCNTs by	Storage capacity (C) with sweep rates (mV)						Discharge capacity (mAh g ⁻¹)
	5	10	20	30	50	100	
HCl	0.22	0.15	0.11	0.05	0.03	0.02	391
HNO ₃	0.35	0.22	0.14	0.09	0.03	0.01	415
H ₂ SO ₄	0.25	0.16	0.09	0.04	0.00	0.00	347
HF	0.35	0.22	0.16	0.11	0.05	0.02	496

by electrochemical system. Polarization was started by potential scanning at the scan rates of 5, 10, 20, 30, 50 and 100 mV s⁻¹ from -1.5 to 0.5 V in the anodic direction and then the scan was reversed in the cathodic direction back to -1.5 V. Cyclic voltammetry of the purified MWCNTs by HCl, HNO₃, H₂SO₄ and HF acids are typically shown at the sweep rates of 20 and 50 mV s⁻¹ (Fig. 6). For all the electrodes in Fig. 6, there is an anodic peak around -0.75 V that involves the oxidation of both Fe to Fe(II) and Fe(II) to Fe(III). Upon reversal of the scan direction, a corresponding reduction peak is appeared around -1.05 V attributed to the reduction of Fe(II) to Fe and Fe(III) to Fe(II). A similar phenomenon has been also reported for Fe₂O₃-loaded carbon by Hang et al. [27]. They found that the purified MWCNTs by HF acid had higher redox peak currents in comparison with the other electrodes, which were also confirmed by our XRD and TGA results (impurities such as Fe–Ni and Fe₃C). The cyclic voltammetry investigations indicated that the small reduction and oxidation peak currents were appeared around the potentials of 0.28 and 0.4 V, respectively. These redox peaks seem to be originated from the transformations of Ni(III)/Ni(II) [28,29]. The voltammograms in Fig. 6 showed that the hydrogen adsorption (a) and desorption (d) peaks were at about -1.35 and 0.15 V vs. Ag/AgCl, respectively. Lombardi and co-workers also reported a similar phenomenon for the purified MWCNTs [22]. Fig. 6 shows that with the increasing of the sweep rate, the peak current intensity increases proportional to the rates. This increase in peak intensity has also been reported by Hsieh et al. for Ni-attached CNTs electrodes [30]. The effects of purified MWCNTs by HCl, HNO₃, H₂SO₄ and HF acids on the adsorption/desorption properties and hydrogen storage capacity using cyclic voltammetry at various sweep rates are summarized in Table 3.

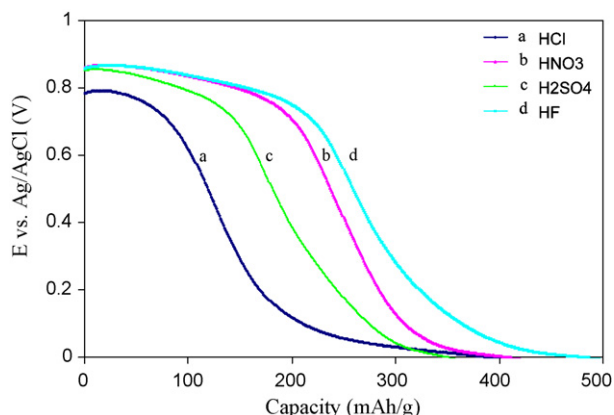


Fig. 7. Discharge curves of the electrodes assembled with the purified MWCNTs by (a) HCl, (b) HNO₃, (c) H₂SO₄ and (d) HF acids.

Table 3 and Fig. 6 show that hydrogen was not stored in the MWCNTs purified by H₂SO₄ acid at the scan rates 50 and 100 mV s⁻¹. In addition, by using the above results, the overall mechanism of the MWCNTs electrodes may be described by the following reactions [8]:

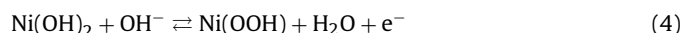
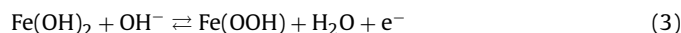


Fig. 7 shows the discharging curves of the purified MWCNTs by HCl, HNO₃, H₂SO₄ and HF acids, in which, the hydrogen storage capacity of the purified MWCNTs by HCl, HNO₃, H₂SO₄ and HF acids are about 391, 415, 347 and 496 mAh g⁻¹, respectively. The hydrogen storage capacities of the purified MWCNTs by the following acids are in ascending order as H₂SO₄, HCl, HNO₃ and HF, which were in accordance with BET and BJH results, probably due to the presence of 1–2 nm micropores in the samples. It has also been reported by Xia et al. [21] for carbon CMK-3. In addition, the hydrogen storage capacities of the purified MWCNTs by H₂SO₄, HCl, HNO₃ and HF acids are in good agreement with graphitization of the MWCNTs obtained by inflection temperature in DSC analyses. This result can be explained by the effect of defective structures on the hydrogen storage (Table 3). Furthermore, the role of catalyst is essential for the process of hydrogen storage [31,32]. It is also true for the purified MWCNTs by HNO₃ and HCl acids. The inflection temperature (Table 1) and micropores volume (Fig. 5 and Table 2) of the purified MWCNTs by both HNO₃ and HCl acids are not much different but rather, their hydrogen storage capacity was considerably different. The catalyst quantity of the purified MWCNTs by HNO₃ is more than those by HCl (see TGA and XRD results). Thus, dissociation rate of H₂O on the surface increased with the increasing of the catalyst's quantity. So, the hydrogen storage capacity of the purified MWCNTs by HNO₃ was more than HCl.

4. Conclusions

The effect of purified MWCNTs by HCl, HNO₃, H₂SO₄ and HF acids on the hydrogen storage capacity was studied. The results indicated that the purified MWCNTs by HF acid had the highest impurities in comparison with the other acids. The inflection temperatures of the purified MWCNTs by the following acids were in descending order as H₂SO₄, HCl, HNO₃ and HF acids.

The obtained results showed that the purified MWCNTs by HF acid had the highest surface area and micropores volume in comparison with the other acids. The results also showed that, under similar sweep rates conditions of cyclic voltammetry and discharge curves, the purified MWCNTs by HF acid had the highest hydrogen storage capacity as compared to the purified MWCNTs by other acids. It was found that the micropores volume in the MWCNTs is very important for hydrogen storage. In addition, the hydrogen storage capacity of the purified MWCNTs by H₂SO₄, HCl, HNO₃ and HF acids was in good agreement with the graphitization of MWCNTs obtained by inflection temperature. Furthermore, our findings showed that the presence of catalyst and defective sites in the MWCNTs influenced the hydrogen storage capacity.

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