Effects of Temperature on Thermodynamic parameters and Carbon Nanotubes Growth Rate on Aluminum Electrode in Electrochemical deposition Process

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Abstract

The optimum process conditions of the electrochemical deposition of carbon nanotubes (CNT) have been established by using developed, cheap and simple system. It has been found that temperature affects on the rate, purity and the yield of CNT obtained in this process. The electrochemical behavior of CNT deposition, kinetic and thermodynamic parameters were also discussed.

Key words: Thermodynamic parameters, Carbon Nanotubes, Electrochemical deposition

Introduction

Since the discovery by Sumio Iijima [1], CNTs has a great deal of attention, and a number of applications have been proposed and demonstrated [2-5] Carbon nanotubes have increasingly been studied in recent years owing to their important properties and a wide variety of potential applications [6]. Elemental carbon has sp^2 hybridization can form a variety of amazing structures [7]. It is well known that graphite carbon can build closed and open cages as a honeycomb atomic arrangement. The nanotubes consisted of one (so called single-walled carbon nanotubes (SWCNTs) with diameters range from~1nm) or several cylindrical layers of rolled up grapheme sheets (so called multi-walled carbon nanotubes (MWCNTs)) with inter layer spacing of (0.34-0.36) nm and diameter to~30nm.The length of nanotube is usually over 1µm.These layers are in most cases helical i.e., the carbon bonds form a spiral around the cylinder [8]. The carbon nanotubes may be used, for example, as catalyst support or semiconductor [9-10]. Several main methods are currently used for synthesis of carbon nanotubes, i.e. carbon synthesis [11]; chemical vapor deposition (CVD)[12] Microwaves technique [13] laser vaporization [14] electrochemical deposition [15].Although the production of CNTs is quite simple, it is up-to-now very difficult to obtain samples of good quality, containing as less contaminating material (nanoparticales, amorphous or graphitic microparticales) as possible, with tubes showing well-defined graphitized layers and tips. The effect of the reaction temperature on growth rate, thermodynamic parameters and on the quality and quantity of carbon nanotubes formed in the electrochemical deposition have been studied.

Experimental

All chemicals were reagent grade or the highest available commercial grade and were used as received. Deionized water was obtained from an Auto still water system (YAMATO Co., Ltd. WG25). CNTs were synthesized by electrolysis using acetonitrile and de-ionized water (1% v/v) as electrolyte. Electrolysis was carried out at atmospheric pressure and the temperature was varied as (288, 298, 308, 318, 328, 338 and 348) K using hotplate stirrer. Carbon nanotubes were deposited onto Aluminum sheet Size (0.5x30x100mm) attached to a copper cathode. Graphite was used as the counter electrode (anode). Before mounting the substrates on the cathode, they were thoroughly cleaned and rinsed with de-ionized water and Ethanol solution respectively. The electrodes were separated by a distance of ~10mm. The applied d.c. voltage between the electrodes was kept ~24 V using a d.c. power supply capable of generating Stabilized voltage (24 V, 24A).6264B DC power supply HEWLETT.PACKARD. The deposition was carried out for ~ (4-6) h. The deposit was characterized by X-ray Diffraction (XRD) (SHIMADZU XRD-6000) Fourier Transform Infra Red spectroscopy (FTIR) (Shimadzu 8400s). Microscope (NIKON ECLIPSE ME600), Scanning Electron Microscope (SEM).

Results and Discussion

In our previous study, we found that the hydrocarbon deposition on the nanocrystalline aluminum oxide hydroxide catalyst is created in two forms: one as single-walled carbon nanotubes in colloidal and precipitant forms and second as a multi-walled carbon nanotubes deposit on aluminum substrate [16] as shown in Figure .1. It was found that acetonitrile can be an effective carbon source for the growth of multi-walled carbon nanotubes. The quantity and quality of these materials depended on different parameters, such as: temperature, reaction time and the $CH_3CN:H_2O$ ratio.

Fig. 2. Illustrates the relation between the CNTs growth with the time at different temperatures varying from (288-348) K and have a similar shapes but with different characteristics and behaviors at all temperatures of experiments. It is an indication that the reaction rate of CNTs deposit formation varies in direct proportion with variation of cell temperature. From this Figure we can see that low temperature deposition processes need about 45 minutes to start flowing ions between electrodes due to preparing aluminum oxide hydroxide film on aluminum substrate, while high temperature processes need about 15 minutes to start CNTs deposition .

In this work, also the relationship between varying temperature of the electrolyte with the rate of CNTs growth and with electrolyte conductivity have been studied as shown in Figures (3 and 4) respectively.

The results indicated that as the temperature rising from 288 K to 318K the CNTs growth rate or electrolyte conductivity caused no significance, while above 318 K the rate of CNTs growth and electrolyte conductivity rise vigorously till 338 K and then drop vigorously with rising temperature because of the growing of the reversible reaction in the electrolyte at high temperatures.

The effect of temperature on the purity of CNTs obtained during this process has been followed by IR spectroscopy. The IR spectra shown in Figure 5(a & b) appeared that CNTs sample prepared at (308 K) the absorption band (1350 cm^{-1}) which related to the absorption of carbonaceous impurities (amorphous carbon) was very strong, and the absorption band (1637cm^{-1}) which related to the absorption of carbon nanotubes surrounded with impurities absorption bands. While in Fig. 4(b) where the sample prepared at (338 K) CNTs absorption band (1637cm^{-1}) clearly appears and impurities absorption bands disappears. That's due to the vigorously rising of the rate of reaction with rising cell temperature and this means that reaction at high temperature consumes all the amorphous carbon in building CNTs while at (308 K) the reaction rate was very slow and there is a large amount of non used amorphous carbon.

The rate constants at temperature range (288-348) K for this process were determined by plotting in current versus. time of CNTs growth, these different results were tabulated in Table(1).

These results indicate that the values of rate constant increase with the increase of temperature as previously shown in figure (2).

This study indicates that the optimum temperature was 338 K and the amount of CNTs decrease after reaching at 348 K.

Plotting ln ($t_{1/2}$) against ln (current) in Fig.6. shows a linear relationship which prove that the reaction is first order.

The kinetic and thermodynamic parameters were studied in this work.

From slop and intercept of Arrhenius plot shown in figure -7- get the activation energy and the pre-exponantional value (A) which equal to 34.8 kJ.mole^{-1} and 194.9 s^{-1} respectively.

From these values the thermodynamic parameters $\Delta^{*}H$, $\Delta^{*}S$ and $\Delta^{*}G$ were calculated according to equation below [17]:

$$\Delta^{*}H = Ea - RT \quad \text{--------------} (1)$$

And $\Delta^{*}S$ from $A = e\,(k_BT/h)\,e^{(\Delta^{*}S/R)}$ ---------- (2)

Therefore $\Delta^{*}G$ is calculated at different temperatures from 288 K to 348 K from equation

$$\Delta^{*}G = \Delta^{*}H - T\Delta^{*}S \quad \text{-------------------------} (3)$$

All results are listed in Table .2.

Entropy changes ($\Delta^{*}S$) calculated from plotting of Gibbs free energy against temperature (Fig. 7.), it was found equal to -209.6 Jmole^{-1}K^{-1}

The positive values of $\Delta^{*}G$ gives an indication of non-spontaneous process as one expected. The process was endothermic due to positive values of $\Delta^{*}H$ (increasing temperature during process) i.e., that higher temperatures are favored for enhanced removal of carbon ions from graphite electrode to growth CNTs. Therefore the $\Delta^{*}S$ was negative and small values suggest the decrease in adsorbate concentration in solid-solution interface indicating thereby the increase in sorbate concentration onto the solid phase, means that the formation of CNTs is less disorder.

Conclusion

From this work, one can conclude that the reaction temperature plays a critical role on the rate, yield and purity for producing CNT. The thermodynamic values indicate the non-spontaneous, endothermic and more regular system.

References

1. Iijima, s. (1991) "Helical microstructures of graphitic carbon", Nature; 354: 56-57.
2. Cao, S.; Tao-Zu, Z.; Lemaitre, M. G.; Xia, M. G.; Shim, M. and Rogers, J. A. (2006) "Transparent flexible organic thin-film transistors that use printed single-walled carbon nanotube electrodes" Applied Physics Letters, 88: 1135111-1135113.
3. Yoo, E.; Habe, T. and Nakamura, J. (2005) "Possibilities of atomic hydrogen storage by cabon nanotubes or graphite materials", Science and Technology of Advanced Materials; 6: 615-619.

4. Sear, K.; Dumee, L.; Schütz, J.; She, M.; Huynh, C.; Hawkins, D.M. and Gray, S. (2010) " Recent developments in carbon nanotubes membranes for water purification and gas separation", Materials; 3: 127-149.
5. Baughman, R.H.; Zakhidov, A.A. and de Heer, W.A. (2002) "Carbon nanotubes- the route toward applications- review ", Sience; 297: 787-297.
6. Morinobu, E.; Takuaya, H.; Yoong, A.K.; Mauricio, T. and Milred, S.; D., (2004): "Applications of carbon nanotubes in the twenty-first century", Phil. Trans. R. Soc. Lond. A 362: 2223–2238.
7. Dong, Q.; Gregory, J.W.; Wing, K.L.; Min-Feng, Y. and Rodney, S.R. (2002) "Mechanics of carbon nanotubes", Appl. Mech. Rev 55: 495-533.
8. Bonard, J.; M.; Forro, L.; Ugate, D.; De Heer, W.A. and Chatelain, A, (1998) "Physics and chemistry of carbon nanostructures", European Chemisrty Chronicale 3: 9-16.
9. Chen, G.X.; Kim, H.S.; Park, B.H. and Yoon, J.S., (2006) "Multi-walled carbon reinforced nanotubes nylon 6 composites" Polymer; 47: 4760–4767.
10. Samal, S.S.; Bal, S. (2008) "Carbon nanotube reinforced ceramic matrix composite-a review" Minerals and Materials Charactization and Engineering; 7(4): 355-370.
11. Babanejad, S.A.R.; Malekfar, R. and Seyyed Hosseini, S.M. R., (2009): "Dispersive Micro Raman Backscattering Spectroscopy Investigation of Arc Discharge Synthesized CNTs Doped by Boron and Nitrogen", Acta Physica Polonica A.; 116: 217-220.
12. Arjmadi, N.; Sasanpour, P. and Rashidian, B., (2009): "CVD synthesis of small-diameter single-walled carbon nanotubes on silicon" Computer Science & Engineering and Electrical Engineering 16(1): 61-64.
13. Kharissova, O.V.; Catanon, M.G.; Pinero, H.J.L. and Mendez, U.O., (2009): "Fast production method of Fe-filled carbon nanotubes"Mechanics of Advanced Materials and Structures, 16: 63-68.
14. Puretzky A. A.; Schittenhelm, H.; Fan, X.; Lance, M.J.; Allard, Jr.L. F. and Geohegan, D.B., (2002): "Investigations of single-wall carbon nanotube growth by time-restricted laser vaporization" The American Physical Society.; 65: 245-425.
15. Pal, A.K.; Roy, R.K.; Mandal, S.K. and Deb, G.B., (2005): Electrodeposited carbon nanotubes thin films", Thin Soild Films.; 476: 288-294.
16. Hussain, D.H.; Rasheed, A.I. and Faisal, A.D., (2010): "Synthesis of carbon nanotubes by electrochemical deposition using Aluminum substrate", Special Edition Researchers of The 6th conference College of Science Al-Mustansiriyah University from 9-10 Februray, Al-Mustansiriyah Journal of Science.; 21(5): 168-174.
17. Laidler, K.J.; Meiser, J.H. and Sauctuary, B.C., (2003): "Phsical Chemistry", 4th Edition Houghton Mifflin Company Boston New York pp 383-394.

Table(1): the values of rate constant.

Temp. K	288	298	308	318	328	338	348
$k_{obs.}s^{-1}$	0.0001	0.00016	0.00026	0.00028	0.00069	0.0008	0.0004
R^2	0.9565	0.9923	0.9471	0.9524	0.9170	0.9300	0.9909

Table (2): Thermodynamic parameters of $\Delta^* H$, $\Delta^* S$ and $\Delta^* G$.

Temp. K	$\Delta^* H$ kJ.mole^{-1}	$\Delta^* S$ J.mole^{-1}.K^{-1}	$\Delta^* G$ kJ.mole^{-1}
288	32.405	-209.10	92.597
298	32.322	-209.39	94.723
308	32.239	-209.66	96.814
318	32.156	-209.92	98.910
328	32.073	-210.19	101.015
338	31.989	-210.44	103.033
348	31.906	-210.68	105.222

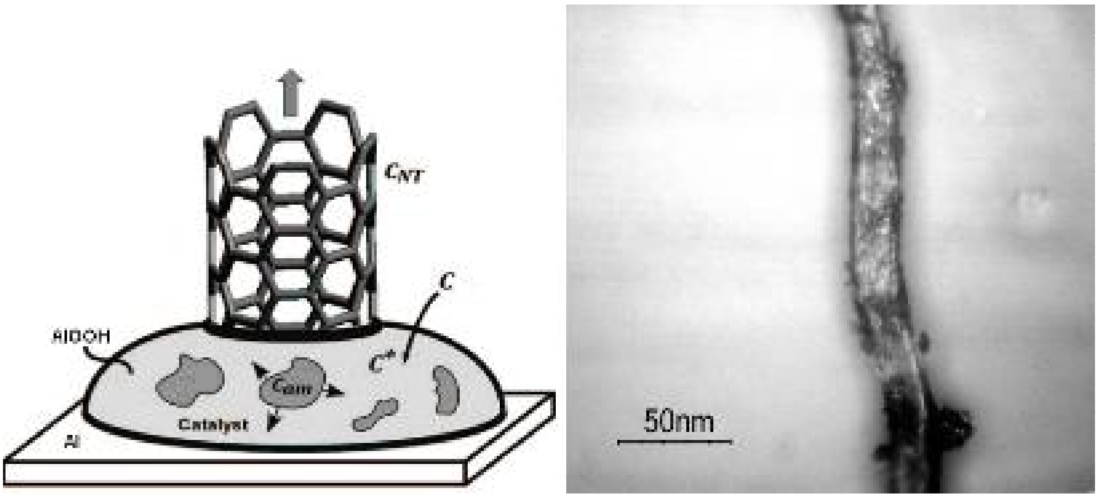


Fig.(1): Schematic diagram and a Photo of CNT deposit on Aluminum electrode form SEM.

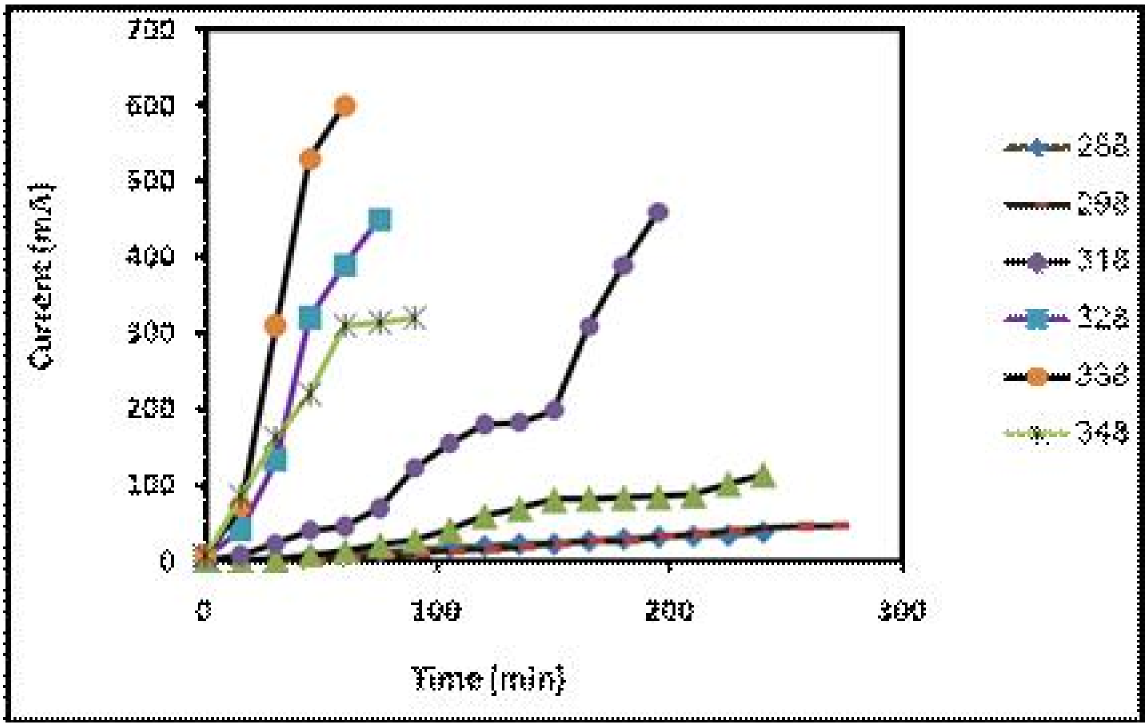


Fig. (2): Relationship between CNTs growth with deposition time of different temperatures (288-348) K.

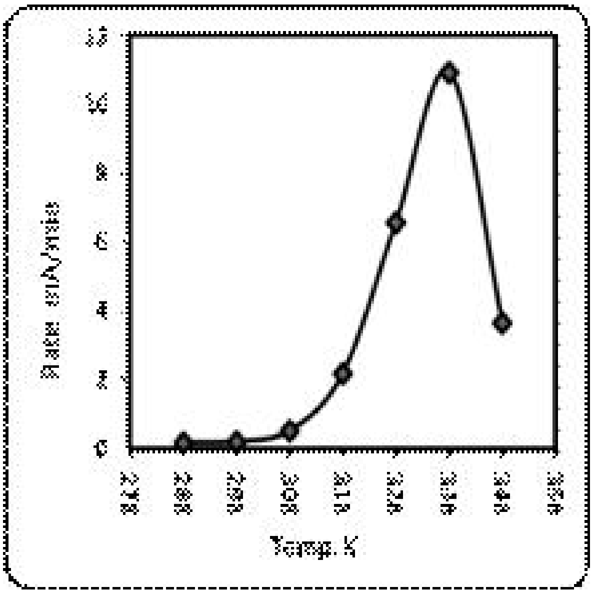


Fig. (3): The effect of temperature on CNTs growth rate during deposition process.

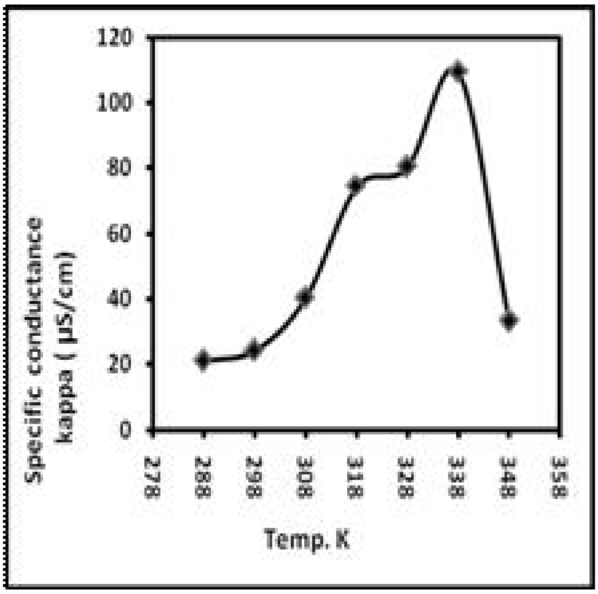
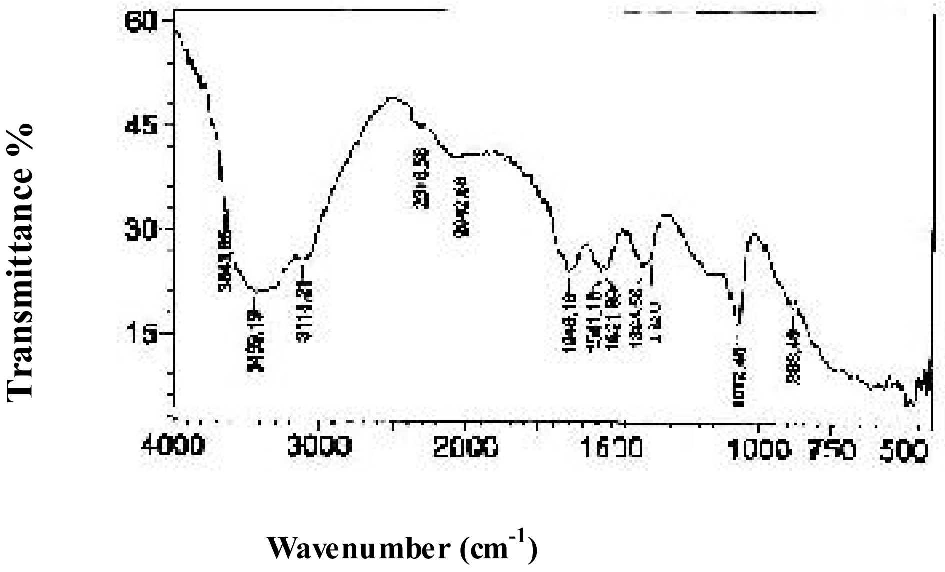


Fig.(4): The effect of temperature on electrolyte conductivity during CNTs growth process.



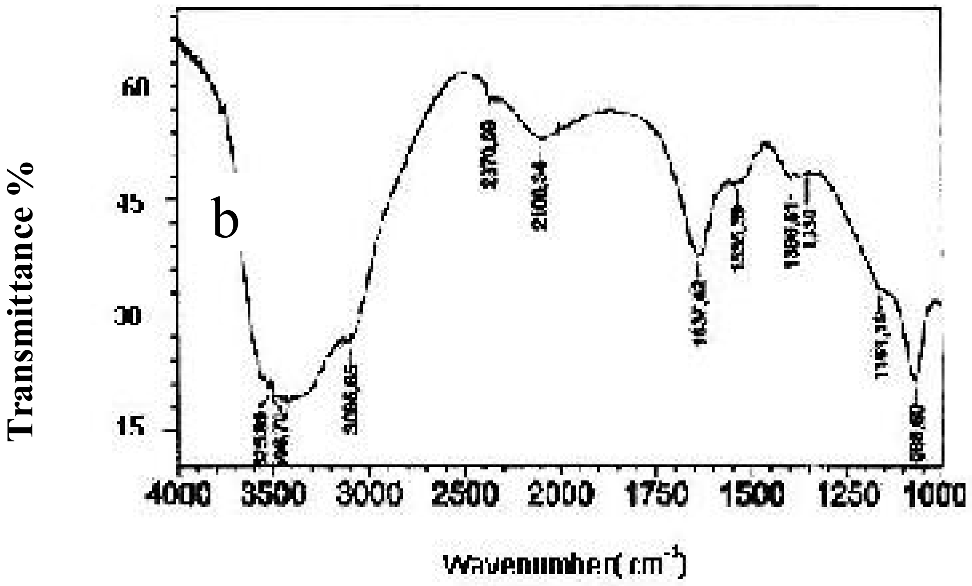


Fig. (5): IR Spectra of prepared CNTs sample (a) at 308 K (b) at 338 K.

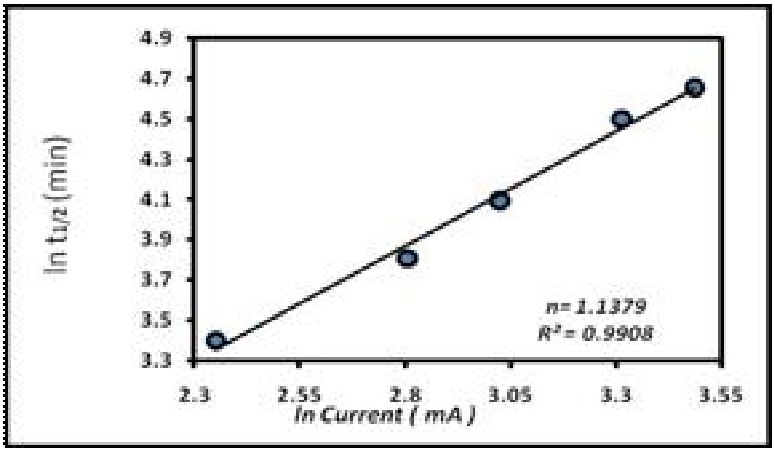


Fig. (6): Relationship between ln $t_{1/2}$ vs. ln current at 288 K.

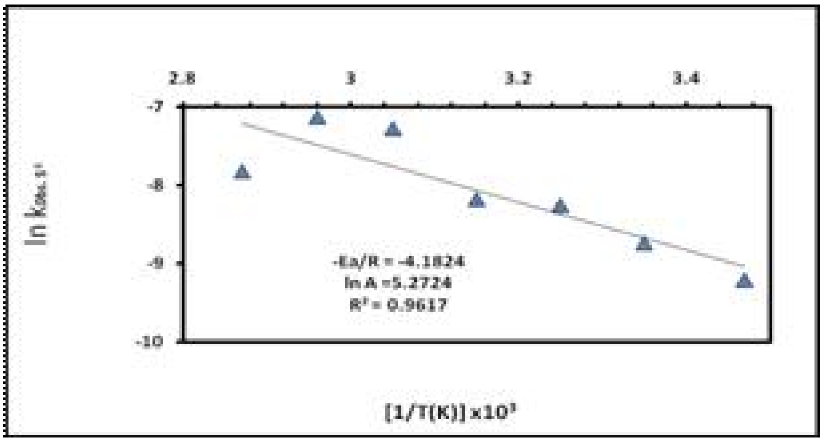


Fig. (7): Plot of Arrhenius relationship for CNTs growth.

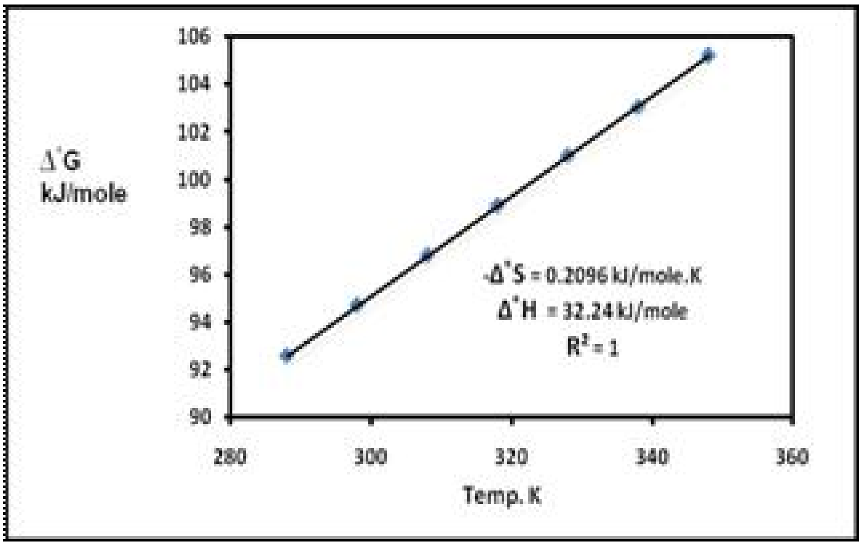


Fig. (8): Changes of Gibbs free energy against temperature.

تأثيرات درجة الحرارة في القيم الثرموديناميكية ومعدل سرعة نمو الأنابيب النانونية للكربون المترسبة على قطب الألمنيوم بطريقة الترسيب الكهربائي

استلم البحث في:11 نيسان 2010
قبل البحث في : 27 أيلول 2010

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الخلاصة

تم في هذا البحث تثبيت ظروف العمل المثلى لترسيب الانابيب النانوية للكربون (CNTs) باستخدام جهاز مطور ورخيص وبسيط في عملية الترسيب الكهروكيميائي للـ(CNTs)،اذ وجد في هذا العمل إن لدرجة الحرارة تأثيرا في سرعة التفاعل والنقاوة وكمية الناتج من الـ(CNTs). ولهذا السبب فإنَ من الظروري التحقق من السلوك الكهروكيميائي لعملية ترسيب الـ(CNT) ودراسة القيم الحركية والثرموديناميكية .

الكلمات المفتاحية : القيم الثرموديناميكية ، الأنابيب النانونية للكاربون،طريقة الترسيب الكهربائي