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Electro-catalytic activity of multiwall carbon nanotube-metal (Pt or Pd) nanohybrid materials synthesized using microwave-induced reactions and their possible use in fuel cells

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Abstract

Microwave induced reactions for immobilizing platinum and palladium nanoparticles on multiwall carbon nanotubes are presented. The resulting hybrid materials were used as catalysts for direct methanol, ethanol and formic acid oxidation in acidic as well as alkaline media. The electrodes are formed by simply mixing the hybrids with graphite paste, thus using a relatively small quantity of the precious metal. We report Tafel slopes and apparent activation energies at different potentials and temperatures. Ethanol electro-oxidation with the palladium hybrid showed an activation energy of 7.64 kJmol⁻¹ which is lower than those observed for other systems. This system is economically attractive because Pd is significantly less expensive than Pt and ethanol is fast evolving as a commercial biofuel.

Keywords

Electro chemical oxidation; Tafel slopes; Platinum and palladium; ethanol; Graphite paste electrode

1. Introduction

Electro-oxidation of methanol, ethanol, formic acid and other small organic molecules has received much attention in recent years because of promising applications in low temperature fuel cells [1]. They are known to provide high energy density and allow the use of liquid fuels rather than hydrogen, thus enabling easy storage [2–7]. Some of the challenges facing this technology are electrolyte crossover to the cathode, high activation over potentials and CO poisoning of the catalyst surface, which is usually platinum [5]. The success of these fuel cells depends upon the development of efficient and inexpensive electro-catalysts with high activity and durability [8, 9]. Extensive research has been carried out to develop advanced electrolytes, active anode catalysts to promote fuel oxidation, and

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to prevent CO poisoning. Moreover, precious metals such as Pt are used as catalysts that are quite expensive, and recent efforts have focused on alternate metals such as Pd as the catalyst.

Nanoscale catalytic materials are attractive due their high surface to volume ratio, and quantum chemical properties. Nanoparticles immobilized multi walled carbon nanotubes (MWNTs) have shown excellent catalytic properties for oxidation of alcohols and acids [10]. Carbon nanotubes (CNTs) are effective supports for nanometal particles (NP), and together they represent hybrid structures (NP-CNTs) that combine the unique properties of both. Consequently, they have attracted much attention due to their promising applications in electronics, catalysis, and biosensors [11]. Several synthetic routes for making NM-CNT hybrid materials have been investigated. These include in situ synthesis of metal NPs on functionalized CNTs, electro-deposition or spontaneous reduction [12] where the NPs are deposited onto CNTs by physical adsorption, polymer-mediated deposition of pre synthesized NPs on functionalized CNTs by electrostatic interaction or self-assembly. The latter makes the nanohybrids compatible with solvents and thus more useful in catalysis and biomedicine [13]. Many of these methods require elaborate procedures that limit their real-world applications. The challenge posed by these techniques is the inability to achieve both uniformly dispersed nanoparticles on the CNT surface and high metal loading [14, 15].

Over the last few years we have developed a novel microwave induced reaction for the functionalization of CNTs [16, 17], the synthesis of polymer and ceramic composites and the formation of CNTs nanohybrids, which have been used as homogeneous catalysts for organic reactions [18] and environmental remediation involving arsenic removal and defluoridation [19, 20]. These have involved solution phase reactions involving functionalized dispersible CNTs leading to the formation of uniformly distributed highly loaded hybrid phase.

Various nanohybrids have been used as modifiers for carbon paste electrode (CPE) [21, 22]. These modified electrodes provide several advantages, such as, ease of fabrication, simplicity in modification, simple surface renewal, low ohmic resistance, wide potential window, and most importantly, low cost [23].

The objective of this work was the development of microwave synthesized Pd and Pt immobilized CNT nanohybrids as electro-catalytic materials for methanol, ethanol and formic acid oxidation. Yet another objective is to explore the possibility of using graphite paste electrode for preparing the composite using the NP-CNT catalyst.

2. Experimental

2.1 Chemicals

Multiwall carbon nanotubes (MWCNT) (OD 20–30nm, Purity 95%) were purchased from Cheap Tubes Inc. Methanol, ethanol, formic acid, sodium hydroxide, and sulphuric acid used in this study were analytical grade (AR). Millipore water having a resistivity of 18.2 MΩ cm was used to prepare the aqueous solutions. All other chemicals were purchased from Sigma Aldrich with purity higher than 95%.

2.2 Synthesis of Catalytically Active Nanohybrids

Carboxylated Multiwall Carbon Nanotubes (MWCNT-COOH) were synthesized using previously published methodology [16, 17]. Carbon nanotubes were functionalized in a Microwave Accelerated Reaction System (Mode: CEM Mars) fitted with internal temperature and pressure controls. Pre-weighed amounts of purified MWCNT were treated with a mixture of concentrated H₂SO₄ and HNO₃ solution by applying them to microwave

radiation at 140°C for 20 min. This led to the formation of carboxylic groups on the surface leading to high aqueous dispersibility. The resultant solid was filtered through a 10µm membrane filter, washed with water to a neutral pH and dried under vacuum at 80°C to a constant weight. The MWCNT-COOH was used to synthesize the nanohybrid Pt-MWCNT and Pd-MWCNT. Typically, 100 mg of the CNTs was reacted with 30 mL of 12.5 mM platinum dichloride (PtCl₂) or palladium dichloride (PdCl₂) ethanol mixture under microwave radiation at 190 °C for 10 min. The product was filtered, washed with 0.5 N hydrochloric acid (HCl) solution and DI water separately and dried at room temperature in a vacuum oven for 12 h.

The NP-CNTs were characterized using a scanning electron microscope (SEM) fitted with an Energy Dispersive X-ray spectrometer (EDX), Thermo gravimetric analysis (TGA), and Fourier Transform Infrared spectroscopy (FTIR). SEM Data was collected on a LEO 1530 VP Scanning Electron Microscopy equipped with an energy-dispersive X-ray analyzer. TGA was performed using a Pyris 1 TGA from Perkin-Elmer Inc. FTIR measurements were carried out in purified KBr pellets using a Perkin-Elmer (Spectrum One) instrument.

2.3 Carbon Paste Electrode Preparation and Electrochemical Measurements

To demonstrate the electro-catalytic activity of Pt-MWCNT and Pd-MWCNT, 0.01grams of the sample was mixed with carbon powder (0.155grams) to form a carbon paste electrode. Significantly lower amounts of the Pt-MWCNT and Pd-MWCNT nanohybrid was used in fabricating the carbon paste electrode used in this study compared to previous reports [24]. These were used in alkaline as well as acidic medium to study electro-oxidation reactions. To ensure that the electrodes are cleaned before each experiment, they were flushed with Millipore water, and electrochemically cycled with 1M H₂SO₄ by anodic sweep from -0.3 V to 1.2 V during which the oxides of the Pt and Pd are formed. This is followed by reverse cathodic sweep during which the oxide is reduced. This process renews the electrode surface and activated the catalyst material.

Cyclic voltammetry (CV) was carried out using an EG&G potentiostat (model 263A) interfaced to a computer through a GPIB card (National instruments). The electrolyte temperature was varied using a temperature controller (JULABO Model F25). A conventional three-electrode electrochemical cell was used for the electro-oxidation studies. A platinum foil of high surface area was used as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The cell was cleaned thoroughly before each experiment and kept in a hot air oven at 100 °C for at least 1 h before the start of the experiment. The chronoamperometry measurements were carried out by the application of a potential pulse of 5 s duration. Currents measured at the end of 5 s of the potential pulse were used for polarization plots and calculation of Tafel slopes.

3. Results and Discussion

3.1 Nanohybrid Characterization

SEM images of MWCNT-COOH, Pt-MWCNT and Pd-MWCNT hybrids are shown in Figure 1(a–c). MWCNTs had diameter in the range of 20–40 nm and the length was about 10–30 µm. There was no detectable change in tube morphology after acid treatment or after hybrid formation, implying that there was minimal damage to the tube structure. Covalently introducing functional groups, such as carboxylic (-COOH) on the carbon nanotube surface enhances their dispersibility resulting in the synthesis of uniform metal nanoparticles on the CNT surface. Pt and Pd nano particles on the CNT surface are seen as bright spots in the SEM images of the hybrid materials as shown in Figure 1(b) and 1(c), the uniformity of the metal nanoparticles on the CNT surface is quite evident from these images. The EDS data shown in Figures 1 (d) and (e) confirmed the presence of large amounts of metal particles on

the surface of the carbon nanotubes in agreement with the TGA data (Figure 3), where the details of metal loading are discussed. From the EDS data of MWCNT-COOH (not shown) it was 5.27% of the carbon atoms were carboxylated.

The FTIR spectrum shown in Figure 2 confirmed the presence of functional groups in MWCNT, MWCNT-COOH, Pt-MWCNT and Pd-MWCNT hybrids. The carboxylic stretching frequency in MWCNT-COOH was seen at 1715 cm^{-1} (COOH); this band was clearly absent from the original MWCNT spectrum. The 3422 cm^{-1} band (O-H) present in MWCNT-COOH spectrum was attributed to the hydroxyl vibration of the carboxylic acid group introduced through functionalization. In all the samples, the peak around 1576 cm^{-1} was assigned to the C=C stretching of the carbon skeleton. The appearance of a new band at 970 cm^{-1} in the Pd-MWCNT spectrum confirmed the presence of Pd in the hybrid. From the spectra of Pt-MWCNT and Pd-MWCNT, it can be seen that the peak at 3422 cm^{-1} belonging to the O-H vibration of carboxylic acid disappeared. The disappearance of the peak of O-H vibration of carboxylic acid was attributed to fact that metals are anchored to the MWCNTs through an esterification process, in line with previous observation [20].

TGA was used to quantify the metal nanoparticle loading in the hybrid materials as shown in Figure 3. The resulting weight above 600°C was attributed to the weight of residual metal or metal oxide. These nanoparticles were found to contain as much as 40.11 % (by weight) of Pt in Pt-MWCNT and 38.93 % (by weight) of Pd in Pd-MWCNT, implying an approximate Metal: Carbon atomic ratio of 4:100 and 7:100 for Pt and Pd respectively. The molar ratios of the metal nanoparticles observed here are over an order of magnitude higher than previously reported value, and consequently a smaller amount of metal-MWCNT nanohybrid was used here [24]. The catalytic activity of the nanoparticles is evident from the TGA profile of Pt-MWCNT, where it altered the thermal stability of the MWCNT. The hybrid degraded at a significantly lower temperature (nearly by 200°C) compared to the purified MWCNT, because Pt catalyzed its oxidation, consistent with previous observation [25].

3.2 Voltammetric Response of Pt-MWCNT and Pd-MWCNT in Acid Medium

A modified cyclic voltammetry approach (based on adsorption/stripping from solution) was used to determine the real surface area of the electrodes. This involved hydrogen adsorption from solution in the potential region prior to hydrogen evolution. The electrochemically active surface area (ECSA) of the electrodes was calculated from the charge measured under the Pt-H and Pd-H desorption peaks in the lower potential region in $0.5\text{M H}_2\text{SO}_4$ as shown in Figure 4. This charge was used to calculate the surface area of platinum [26] and palladium [4, 27, 28] in the nanohybrids. The charge under the voltammetric peaks for hydrogen adsorption or desorption (after correcting for the double layer charging current) was assumed to correspond to the adsorption of one hydrogen atom on each metal atom on the surface (metal-hydrogen). The charge associated with the hydrogen adsorption for platinum is $210\text{ }\mu\text{C cm}^{-2}$ and the charge associated with desorption of oxide in the case of palladium oxide [28] is $424\text{ }\mu\text{C cm}^{-2}$. Using this data, and based on Figure 4(i) and 4(ii), the ECSA for platinum and palladium in the nanohybrid modified carbon paste electrodes were calculated to be 0.734 cm^2 and 0.3846 cm^2 respectively. In Figure 4(i), a clear peak around -0.2V during the forward scan corresponded to hydrogen desorption on platinum surface. A Peak around 0.5V corresponded to oxidation of platinum surface and this platinum oxide stripping peak was seen around 0.5V during the reverse scan. This oxide stripping peak during reverse scan was used for surface area calculations as discussed above. Hydrogen adsorption peak around 0.15V was observed due to the overlap of hydrogen evolution peak. Palladium nanoparticles recorded in $0.5\text{M H}_2\text{SO}_4$ showed anodic peaks at around -0.15V and 0V in the forward scan of Figure 4(ii). These were attributed to Hydrogen adsorption, and absorption reflecting the amount of the active sites available on the electro-catalyst for

the oxidation reaction. A peak at around 0.5V pointed to the oxidation of metal surface [29]. During the reverse scan palladium oxide stripping was accompanied by a peak around 0.4V and a peak after 0V corresponded to hydrogen desorption.

3.3. Catalytic Activity of Pt-MWCNT and Pd-MWCNT Electrodes

Figure 5(i) shows the methanol electro-oxidation voltammograms for Pt-MWCNT in 0.5M NaOH and for the increase in methanol concentration by 0.2M at each step. The onset potential for methanol electro-oxidation was found to be around -0.6 V. Maximum current of 3.9 mA cm^{-2} appeared at -0.19 V corresponding to the oxidation of methanol on the electro-active surface. The onset potential value reported here was lower than those reported earlier [30, 31]. The peak in reverse scan at a potential of -0.45V corresponded to the reduction of PtO formed during the forward scan. Ethanol electro-oxidation voltammograms for the Pt nanohybrid in 0.5M NaOH and for the increase in ethanol concentration by 0.2M at each step is shown in Figure 5(ii). The onset potential for ethanol electro-oxidation, at about 3% of the peak current was found to be around -0.62 V, which was comparable to those previously reported [32, 33] and a maximum current of 14 mA cm^{-2} appeared at -0.18 V. Figure 5(iii) shows the methanol electro-oxidation voltammograms in 0.5M H_2SO_4 and for the increase in methanol concentration by 0.2M at each step. The onset potential for methanol electro-oxidation was found to be around 0.185 V and a maximum current of 0.419 mA cm^{-2} appeared at 0.656 V during the anodic scan. Onset potentials for this system were comparable to those previously reported [1, 2, 9, 26, 27]. In fact it occurred at a potential more negative than previously reported [8] MWCNT nanohybrids, indicating better catalytic activity for methanol oxidation in acid medium. Anodic peak in the forward scan corresponded to the oxidation of methanol that occurred at a potential 150mV, which was more negative than previously reported [6]. The anodic peak during reverse scan, corresponded to the removal of incompletely oxidized carbonaceous species formed during forward sweep appeared at 0.44V which was at a 160mVs more negative potential than that reported earlier [6].

Figure 6(i) shows the CVs for methanol electro-oxidation reaction on Pd-MWCNT electrode in 0.5M NaOH when the methanol concentration was increased by 0.2M at each step. The onset potential for methanol electro-oxidation was found to be around -0.496 V, which was comparable to the values reported [30]. The maximum current of 1.87 mA cm^{-2} at -0.138 V in the forward peak corresponded to the oxidation of methanol reflecting the electro-catalytic activity of the nanohybrid electrode. Ethanol electro-oxidation voltammograms for Pd-MWCNT in 0.5M NaOH and for increase in ethanol concentration by 0.2M at each step is shown in Figure 6(ii). The onset potential for ethanol electro-oxidation at about 3% of the peak current was found to be around -0.54 V and was comparable to those reported earlier [34, 35]. The maximum oxidation current of 2.12 mA cm^{-2} was measured at -0.022 V. Potentials beyond this would have decreasing currents owing to the formation of Pd(II) oxide layer on the electrode surface, thus making the electrode ineffective for ethanol adsorption resulting in negligible ethanol oxidation. During the reverse scan the anodic peak around -0.6V corresponding to the oxidation of the adsorbed molecules during the forward sweep. The increase in currents beyond 0.4V during forward scan was due to the oxidation of Palladium to PdO.

Figure 6(iii) shows the formic acid electro-oxidation voltammogram in 0.5M H_2SO_4 and for increase in formic acid concentration by 0.2M at each step. Figure 6(iii) shows the peak around 0.6V signifying CO pathway for formic acid oxidation reaction [36]. The magnitude of the anodic peak in the region of 0.3V in the reverse scan reveals that the formic acid oxidation occurred essentially by direct pathway [29, 36].

3.4 Activation Energy (E_a) Determination

Arrhenius plots ($\log I$ vs $1000/T$) [1, 6] for methanol, ethanol and formic acid oxidations at different potentials in alkaline and acid media, near the foot of the cyclic voltammogram are provided in supporting information (S1–S7). The linear relationship observed from these plots indicates that the fundamental mechanism of electro-oxidation remains same at all the temperatures.

The activation energy, E_a , in the conventional Arrhenius formula is as follows,

$$k(T) = Ae^{-E_a/RT}$$

where $k(T)$ is the rate constant, A is the pre-exponential factor, T is the temperature and R is the gas constant. The activation energy E_a may be obtained from the currents measured at different temperatures using the formula.

$$E_a = R \frac{d(\ln I_0)}{d(1/T)}$$

The apparent activation energies were calculated from the slope of the curves in the Arrhenius plots (slope = $-E_a/2.303R$). The activation energy values have been labeled adjacent to their respective plots and the average values are tabulated in Table 1. The methanol oxidation reactions in alkaline medium for platinum and palladium composites are comparable to those in the literature. The average E_a values for ethanol oxidation reaction were significantly less for both platinum and palladium [34, 35] composites than those previously reported. While in acid medium using the platinum composite, the average E_a is much less for the methanol oxidation [1, 6]. Formic acid oxidation on platinum composite showed much lower E_a than reported earlier [37] and average E_a values for palladium composites were comparable with literature values [38].

3.5 Tafel Plot Analyses

Tafel slopes [35] are essentially the slopes of the polarization plots and they provide important insight into the reaction mechanism. Under the present condition where the electron transfer processes led to irreversible oxidation of the reactive species like methanol, ethanol and formic acid, the kinetic data could directly be obtained from the steady state current-voltage measurements. The analysis based on the Tafel equations are as follows.

$$\text{For a cathodic reaction, } \log |I| = \log I_0 - \alpha_c n F \eta / 2.303 RT$$

$$\text{While for an anodic reaction, } \log |I| = \log I_0 + \alpha_a n F \eta / 2.303 RT$$

Where I is the total current density, I_0 is the exchange current density, α_c and α_a are the respective cathodic and anodic Tafel slopes and η is the overpotential, which is defined as the deviation of applied potential from the equilibrium potential. The plot of $\log(I)$ versus η is known as the Tafel plot, given in supporting information (S8–S9), and the values of α_c , α_a are obtained from its slope. Based on the values of Tafel slopes, it was concluded that Pt-MWCNT and Pd-MWCNT showed excellent electro-activity and the values reported here were lower than 120 mV dec^{-1} , reported in the literature [39]. This value corresponded to one electron transfer. However, in case of higher alcohol oxidation, additional complications

arise as a consequence of the adsorption of many reaction intermediates, causing surface poisoning [1]. At the same time, the Tafel slopes can act as reliable indicators for understanding the reaction process and its temperature dependence. Tafel slope values at different temperatures near the foot of the cyclic voltammogram for methanol oxidation reaction with platinum and palladium nanohybrids in alkaline medium are given in Table S1. From kinetic theory, Tafel slopes around 120 mV dec^{-1} implies that the rate determining step for methanol oxidation reaction is splitting up of the first C–H bond of methanol molecule with the first electron transfer [6]. The Tafel slopes for methanol oxidation in acid medium for Pt-MWCNT are presented in Table S2. Even for this system, average slope was less than 120 mV dec^{-1} indicating that Pt nanohybrid in graphite paste electrode acted as a suitable electrode for methanol oxidation reaction in acid medium. Nanohybrids of Pd in alkaline and Pt in acid medium provided Tafel slopes that initially increased with temperature and then decreased at higher temperatures. This may be due to quick removal of the adsorbed intermediates at higher temperatures leaving more surface sites for reaction to occur. At lower temperature, the reaction rate was insufficient to completely cover the surface.

4. Conclusions

The microwave induced processes were excellent methods for fast synthesis of electro-catalytic materials. Both Pt-MWCNT and Pd-MWCNT were excellent catalysts for the electro-oxidation of methanol, ethanol and formic acid with potential applications in fuel cells. The uniqueness of the method consists in the use of graphite paste electrode mixed with the nanohybrids, thus requiring relatively small quantity of the catalyst material. The electrode so prepared exhibited excellent stability and reproducible concentration and temperature profiles. Activation energy values were low for ethanol oxidation with palladium nanohybrids which is an advantage due to the low cost of former compared to Pt, and ethanol is easily available from bio mass. The Tafel slopes confirmed that palladium composite in alkaline medium and platinum composite in acid medium were suitable electro-catalysts for methanol oxidation reaction, which can be used for direct methanol fuel cells.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 2. FTIR Data for (a) MWCNT, (b) MWCNT-COOH, (c) Pt-MWCNT, and (d) Pd-MWCNT

Figure 3. TGA data for (a) MWCNT, (b) MWCNT-COOH, (c) Pt-MWCNT, and (d) Pd-MWCNT

Figure 4. Cyclic voltammogram for (i) Pt-MWCNT and (ii) Pd-MWCNT, in the carbon paste electrode in 0.5M H_2SO_4 . Scan rate: 100 mV S^{-1} .

Figure 5. Cyclic voltammograms for Pt-MWCNT in carbon paste electrode in: (i) 0.5M NaOH with various methanol concentrations, (ii) 0.5M NaOH with different ethanol concentrations, (iii) 0.5M H₂SO₄ and at different methanol concentrations. Where a-0M; b-0.2M; c-0.4M; d-0.6M; e-0.8M; f-1M. Scan rate: 100mV S⁻¹.

Figure 6.

Cyclic voltammogram for Pd-MWCNT in carbon paste electrode in: (i) 0.5M NaOH and with various methanol concentrations, (ii) 0.5M NaOH and at various ethanol concentrations, (iii) 0.5M H₂SO₄ and at different formic acid concentrations. Where a-0M; b-0.2M; c-0.4M; d-0.6M; e-0.8M; f-1M. Scan rate: 100mV S⁻¹.

Table 1

The average E_a values for the potential ranges studied for the nanohybrid modified carbon paste electrodes are as follows.

	Pt-MWCNT	Pd-MWCNT
Methanol	17.88 kJmol ⁻¹	10.10 kJmol ⁻¹
Ethanol	25.53 kJmol ⁻¹	7.64 kJmol ⁻¹
Formic acid	20.32 kJmol ⁻¹	29.15 kJmol ⁻¹
Methanol (acid)	14.1 kJmol ⁻¹	---