New borohydride fuel cell with multiwalled carbon nanotubes as anode: A step towards increasing the power output

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Abstract

A borohydride fuel cell has been constructed using a platinized multiwalled carbon nanotube (MWCNT) anode and an air cathode having an anionic exchange membrane separating the anode and cathode. The MWCNT was functionalized with carboxylic acid under nitric acid reflux. Platinum metal was subsequently incorporated into it by galvanostatic deposition. The platinized functionalized MWCNT was characterized by thermogravimetric analysis, Fourier transform infrared spectrum, scanning electron microscope and X-ray diffraction. The fuel cell produced a voltage of 0.95 V at low currents and a maximum power density of 44 mW cm^{-2} at room temperature in 10% sodium borohydride in a 4 M sodium hydroxide medium. Another borohydride fuel cell under identical conditions using carbon as the anode produced a cell voltage of 0.90 V and power density of about 20 mW cm^{-2}. The improved performance of the MWCNT is attributed to the higher effective surface area and catalytic activity.
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1. Introduction

There has been an active interest in developing a borohydride fuel cell that is amenable to room temperature operation [1,2]. It has been constructed with a number of different materials as anodes. They range from Ni (porosity 80%) [3] to Pt, Pd or Ni$_2$B [4,5]. But none of these electrodes gave a satisfactory power output. Amendola et al. [1] developed a borohydride fuel cell with Au (97%)–Pt (3%) alloy electroplated onto a carbon cloth for achieving a current density of 20 mA cm^{-2} at room temperature and ambient pressure. The historical developments in the electrochemistry of borohydride that are relevant to the borohydride fuel cell are discussed in the literatures [6–20].

The power output of a borohydride fuel cell arises from the direct oxidation of the borohydride ion in the alkaline medium. However, it produces concurrent evolution of hydrogen by hydrolysis of borohydride that has been studied in detail [8–10]. Several metals have been found to catalyze this hydrolysis [13–15]. At high concentrations of hydroxide ion or by adding thiourea, the hydrogen evolution has been reduced or eliminated [17].

A borohydride fuel cell giving a higher power density will lead to a more compact power unit [18]. For a cell with two times higher power density, the required number of cells would be reduced by a factor of 2. Thus not only the size but also the maintenance costs will be reduced as the total number of serviceable fuel cells are reduced by a factor of 2. The present paper is aimed at improving the power output of a borohydride fuel cell at room temperature and atmospheric pressure by using platinized multiwalled carbon nanotube MWCNT that has a tubular structure with an area of 1000 m^2 g^{-1} and a conductivity of 10^7 S cm^{-1} [21–26].

2. Experimental

2.1. Chemicals

Sodium borohydride was procured from the Aldrich chemical company and was used as received. Sodium hydroxide was a Baker reagent grade. MWCNTs were obtained from Helix

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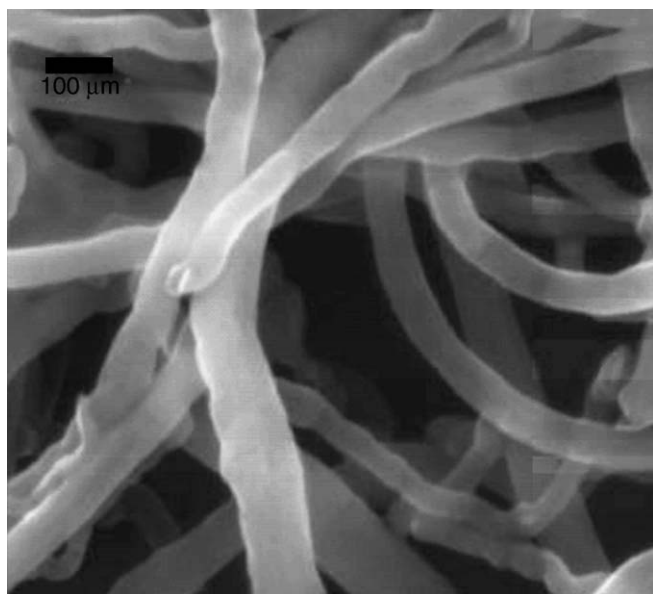
Fig. 1. SEM of MWCNT.

solutions (CVD) or Deal (electric arc method). Fig. 1 shows an SEM of the Helix samples used in the experiments. The SEM of the Deal sample is similar except the tubes were shorter. The samples were purified by refluxing with 6 M nitric acid for a period of 24 h at 90 °C. The mixture was cooled to room temperature and washed thoroughly with de-ionized water (20 °C) to remove traces of acid in the sample. The sample was air dried at 100 °C for 24 h before the experiments [27].

2.2. Electrodes

The anode was constructed using the functionalized MWCNT or unfunctionalized MWCNT or platinized functionalized MWCNT with a paraffin oil binder [28]. A commercial air electrode (Millennium, Fuelcells store.com) was used as the cathode.

2.3. Cell configuration

The cell consisted of an anode (A) and a cathode (C) (Fig. 2) in a 10% sodium borohydride solution made in a 4 M sodium hydroxide with the anode placed in a vertical configuration. The
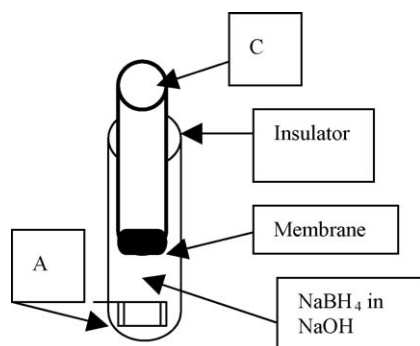

Fig. 2. Experimental design of the fuel cell.

cathode air electrode was immersed into the tank of borohydride solution. Platinum or stainless steel covered with carbon nanotubes acted as the current collector and it was bonded to the anode. The current collector was completely shielded from coming into contact with the solution. The cell had a very small internal resistance (0.5 Ω).

2.4. Power measurements

The power density measurements were done by applying constant potentials from −0.95 to −0.10 V for 1 min across the borohydride-air cell. The power densities were calculated from the experimentally measured current densities and applied potentials.

2.5. Functionalization of MWCNT

About 1 g of MWCNT is taken in a round-bottomed flask and to it about 25 ml of 60% nitric acid was added. The flask was fitted with a condenser and refluxed at about 90 °C for a period of 12 h. After this period, the mixture was cooled to room temperature and washed with distilled water (20 °C) several times until all the acid has been removed. It was filtered and then air-dried for 3 h at 80 °C. The functionalized MWCNTs were characterized by FTIR spectroscopy and TGA.

2.6. Characterization of MWCNT

The carbon nanotubes were characterized by thermogravimetric analysis (TGA). A TA instrument (TGA 2050) was used with a temperature ramp of 5 min. A higher slope ($0.75\% \, °C^{-1}$ versus $0.86\% \, °C^{-1}$) in the weight loss region is observed with functionalized MWCNT. This suggests a smaller weight change with respect to temperature and could be due to the carboxylic end groups acquired during the functionalization. It would be harder to oxidize the carboxyl groups than to oxidize pure carbon, causing the degradation time to increase with temperature.

2.7. FTIR characteristics of functionalized MWCNT

A Biorad Excalibur series FTS 3000 instrument using diffuse reflectance cell was used. The functionalized tubes showed broad bands in the range of 1700–1800 and 3000–3400 cm^{-1} that were absent in the starting tubes. These bands are assigned to C=O group and carboxylic O–H stretches, respectively.

2.8. Platinization of functionalized MWCNT

Cyclic voltammetry of chloroplatinic acid on the functionalized MWCNT showed a cathodic peak at $E_{pc} = 0.30$ V versus saturated calomel electrode (SCE) and a complementary anodic peak $E_{pa} = 0.39$ V versus SCE. The cathodic peak potential is shifted towards a more positive value at this electrode as compared with Pt with an $E_{pc} = 0.14$ V [29]. Furthermore, at the Pt electrode no complementary anodic peak appears in the cyclic voltammetric curves. Thus the appearance of a reversible peak with the functionalized MWCNT electrode suggests that it may

Table 1
Optimization of platinum deposition on functionalized MWCNT[a]

Deposition duration (min)	Maximum current density from load curves (mA cm^{-2})
30	8.57
60	68.82
90	180.21
120	198.45
150	215.58
180	233.45
240	251.52
270	251.00
300	251.52

[a] Medium: 1.2 mM chloroplatinic acid in 0.5 M H$_2$SO$_4$. Counter electrode is platinum plate. Open circuit voltage is 0.94 V in all cases.

be caused by the complexation of the chloroplatinic ion to the acid functionality on the electrode. The anodic peak current decreases upon repetitive cycling.

The platinization of functionalized MWCNT was carried out galvanostatically at 5 μA for different times (see Table 1). After each deposition, the MWCNT was used in the borohydride fuel cell for measuring the open circuit potential and the current density it produced in the borohydride fuel cell using various loads. The optimization of the platinum content was done at a stage when the current density value reached a constancy for two different deposition times. Table 1 gives the measured open circuit voltages and current densities reached in the borohydride fuel cell under maximum load for different deposition times of platinum. We observed a leveling effect for a deposition time of 240 min. The presence of platinum in the functionalized MWCNT was confirmed by (A) X-ray diffraction analysis (XRD) and (B) scanning electron microscope (SEM) and energy dispersive spectroscopy X-ray microanalysis (EDAX).

2.9. XRD analysis

A Philips XRD spectrometer using Cu Kα radiation source was used. The sample prepared by platinization of functionalized MWCNT showed 2θ diffraction peaks of platinum (1 1 1), (2 0 0) and (2 2 0) planes. The sample before platinization did not show these diffraction peaks. Functionalized MWCNT showed 2θ diffraction peaks of nanotubes (0 0 2), (1 0 0) and (0 0 4) arising from graphite lattice. These features are in agreement with the reported values in the literatures [30–32].

2.10. SEM and EDAX analysis

The SEM of the platinized MWCNT shows a reflective shiny surface of carbon. In order to confirm the presence of platinum, EDAX analysis was carried out and it showed a peak at 2.1 keV that matches with the reference value for the platinum metal.

3. Results and discussion

The cyclic voltammetric oxidation of sodium borohydride in 4 M KOH electrolyte shows a well-defined peak at plat-

inum electrode at $E_{pa} = -0.40$ V. The features observed here are similar to the one reported in the literatures [14–17]. The borohydride cyclic voltammetry at MWCNT, functionalized MWCNT and platinized functionalized MWCNT were examined at different concentrations (0.15–1.20 mM) of borohydride. In these experiments, the concentrations have been kept low to fulfill the condition of diffusion-controlled oxidation of the electro active species (BH$_4^-$) relative to the electrical migration of the ions in the medium. This is a primary condition to be fulfilled in the theory of cyclic voltammetry [34]. Although the oxidation of borohydride is ill defined for MWCNT and functionalized MWCNT, cyclic voltammetric curves with platinized MWCNT are well defined and the pattern is identical to that observed with a platinum metal electrode. The current function data for the peak at $E_{pa} = -0.40$ V has been analyzed for an understanding of the nature of the borohydride oxidation. The experiments were carried out with 5, 10, 20 and 40 mg of sodium borohydride dissolved in 20 ml 4 M KOH. The data showed near independency of current function values with increasing sweep rate except at very slow sweep rates. The current function shows constancy beyond 20 mV s^{-1} with increasing sweep rate. If the electrochemical reaction is purely diffusion controlled, one would expect the current function to be constant. The observed deviation could be caused by one of two factors. At slow sweep rates, if convective currents are operating due to density gradients around the electrode surface, then it could produce a deviation. Alternatively, a chemical equilibrium that exists in the alkaline medium has been discussed earlier [8,9,12]; in this medium the borohydride ion is expected to be in equilibrium with BH$_3^-$ and the supply of the borohydride ions to the electrode is controlled by this equilibrium. Because of the kinetics, the current function value will depend on the sweep rate in the electrochemical experiment. At sweep rates beyond 20 mV s^{-1}, a diffusion-controlled process with negligible contribution from the preceding reaction could cause the current function to remain constant with increasing sweep rate. When the sweep rates are below 20 mV s^{-1}, both the processes are involved for the deviation from constancy to occur. The cyclic voltammetric behavior for the equilibrium situation is well discussed in the literatures [33,34].

3.1. Load curves for different borohydride fuel cells

We compared the results of the load curves for the different anodes in borohydride fuel cells. The performance of the functionalized MWCNT or unfunctionalized MWCNT as the anode in the borohydride fuel cell is inferior to the platinized MWCNT suggesting the requirement for platinum on the carbon nanotubes for efficient performance of the borohydride fuel cell. The performance characteristics of the platinized MWCNT and platinized functionalized MWCNT as anodes in the borohydride fuel cells are given in Table 2. The load curves were recorded for the fuel cells at room temperature using platinized functionalized MWCNT (corresponding to 90 μg cm^{-2}) and platinized MWCNT (corresponding to 90 μg cm^{-2}) in 10% NaBH$_4$ in 4 M KOH. The platinized functionalized MWCNT gave a decisively higher power output (see Table 2). The power output data

Table 2
Current and power densities of a borohydride-air cell at room temperature and ambient pressure for different applied cell potentials

Cell potential (V)	Current density (mA cm^{-2})	Power density (mW cm^{-2})
A		
0.90	1.93	1.73
0.85	10.0	8.50
0.80	20.1	16.0
0.38	41.2	15.5
0.10	103.3	10.3
0	170.0	
B		
0.95	8.70	8.2
0.83	24.1	20.0
0.60	66.6	39.9
0.45	98.7	44.4
0.20	160.0	32.0
0.10	204.0	20.4
0	230.0	
C		
0.90	2.5	2.3
0.80	7.8	6.2
0.50	38.0	19.2
0.40	50.0	20.0
0.10	68.1	6.80
0	152.0	

Data obtained with—A: platinized MWCNT; B: platinized functionalized MWCNT; C: carbon containing Au–Pt [1].

obtained with this anode can be compared with that using carbon containing Au–Pt [1]. Platinized functionalized MWCNT gives 180% higher current and about 5% more voltage output. The power density of this borohydride fuel cell is higher by about 200%. Several interesting aspects were revealed in this work. The experimentally observed higher power density with platinized functionalized MWCNT as compared with the unfunctionalized MWCNT (by a factor of 2.7) can be attributed to the catalytic activity of the metal from the introduction of carboxylic acid functionality onto MWCNT. Several previous studies have shown that the carboxylic acid complexes with platinum [35–38] may be a result of a reaction between functionalized carbon nanotubes and chloroplatinic acid during the incorporation of platinum into the nanotubes. With unfunctionalized MWCNT such a coordination is absent. Thus the use of functionalized MWCNT as an anode in the borohydride fuel cell can produce significantly higher power density that is not achievable with the graphite anode.

The borohydride fuel cell using a platinized functionalized MWCNT provides an opportunity to enhance the performance characteristics that will help in fuel cell stacking (a number of individual cells that are connected to boost the power output). Based on the present work, for an anode surface area of 125 cm^2, the borohydride fuel cell (44 mW cm^{-2}) is expected to provide 5500 mW power output in 10% sodium borohydride solution at room temperature and under atmospheric pressure. The power density of each cell under operating experimental conditions would be 550 W kg^{-1} and 550 W l^{-1}. These power density values are comparable with a proton exchange membrane fuel cell

(PEMFC) stack of eight cells giving 967 W kg^{-1} or 846 W l^{-1} [39] or stack of 21 cells giving a power output of 700 W using an electrode area of 100 cm^2 [40]. In neither of the fuel cells a goal of achieving 1000 W l^{-1} (USDOE set goal) has yet been reached. However, scope for achieving this goal exists with the MWCNT described here.

4. Conclusions

Cyclic voltammetric oxidation of borohydride on a platinized functionalized MWCNT is very similar to oxidation on a platinum electrode. Platinum was electrodeposited onto functionalized MWCNT and was subsequently characterized by XRD, SEM and EDAX. The use of platinized functionalized MWCNT as an anode in the borohydride fuel cell with an air cathode resulted in a maximum power density of 44 mW cm^{-2} and a voltage of 0.95 V at low currents with negligible hydrogen evolution at room temperature and atmospheric pressure. The performance of this fuel cell is found to be superior to a graphite-based fuel cell. With platinized unfunctionalized MWCNT as the anode, the power density is about 2.7 times lower suggesting a higher catalytic activity of the functionalized MWCNT.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jpowsour.2005.12.049.

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