



Electro-catalytic oxidation of methane at multi-walled carbon nanotubes-Nafion/nickel hydroxide modified nickel electrode

Jie Qiao^{a,b}, Shengnan Tang^a, Yanni Tian^a, Shaomin Shuang^a, Chuan Dong^{a,*}, Martin M.F. Choi^{c,**}

^a Research Center of Environmental Science and Engineering, School of Chemistry and Chemical Engineering, Shanxi University, Taiyuan 030006, PR China

^b Shanxi Medical University, Taiyuan 030001, PR China

^c Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, Hong Kong, China

ARTICLE INFO

Article history:

Received 15 May 2008

Received in revised form 3 February 2009

Accepted 27 February 2009

Available online 19 March 2009

Keywords:

Methane

Nickel modified electrode

Nafion

Multi-walled carbon nanotubes

ABSTRACT

A novel chemical modified nickel (Ni) electrode based on multi-walled carbon nanotubes (MWCNTs), Nafion film and nickel hydroxide has been successfully fabricated for methane (CH₄) detection at ambient conditions. The morphology of the MWCNTs–Nafion/Ni(OH)₂ film was characterized by transmission electron microscopy and the electrochemical properties of the Ni modified electrode were studied by cyclic voltammetry. The MWCNTs–Nafion/Ni(OH)₂–Ni electrode showed good catalytic effect on the oxidation of CH₄ in 1.0 M NaOH. In addition, the modified electrode was free from nitrogen and oxygen interferences. When differential pulse voltammetry was applied to the MWCNTs–Nafion/Ni(OH)₂–Ni electrode, a good linear relationship between the oxidation peak current (*i*) and CH₄ concentration (*C*_{methane}) was obtained: $i = 1.841C_{\text{methane}} + 46.25$, where *i* is in μA and *C*_{methane} is in 0.0–16.0% (v/v). The relative standard deviation for detection of 3.0% (v/v) CH₄ was 1.80% (*n* = 5). The proposed Ni modified electrode is anticipated to provide a promising technique to detect CH₄ at ambient conditions.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Methane (CH₄) is a major component of the widely used natural fuel gas in industry and private households. It can be released from the walls of coalmines. Explosion will occur when its concentration in air reaches to 5–16% (v/v). Therefore the monitoring of CH₄ in coalmines is very important for safety reasons. In addition, it is also a greenhouse gas which is produced continuously by the anaerobic oxidation of organic materials and needs to be monitored. However, CH₄ is relatively difficult to detect at ambient conditions as its chemical reactivity is low. The commonly used techniques for CH₄ detection include gas chromatography (GC) [1–9], semiconductor devices [10–21], optical fiber sensors [22], electrochemical methods [23–37], and biochemical methods [38,39]. Electrochemical methods are the most advantageous amongst all these techniques because they are simple, fast and sensitive and are applicable for in situ real-time analysis.

To date most electrochemical CH₄ sensors are oxides-based and work only at relatively high temperatures so that better sensitivity of detection can be achieved. For direct electrochemical measurement of CH₄ at ambient conditions, electrode materials of transition metals such as nickel (Ni) or Ni alloys have to be used in strong alkali-

line working media. It has been reported that anodic oxidation of these electrodes in strong alkaline media produces a metal hydroxide layer that can react with CH₄ via an electro-catalytic pathway [40], but the results are still not satisfactory. Thus, there is still a need to develop other sensing materials that can detect CH₄ at room temperature.

Recently carbon nanotubes (CNTs) [41] are emerging as a promising material for electrochemical detection, attributing to their unique characteristics such as high mechanical strength and modulus [42]. It is possible that new electrochemical sensors and novel electro-catalytic materials [43] can be fabricated with CNTs modified electrodes as the subtle electronic property of CNTs can promote electron transfer in an electrochemical reaction. This characteristic has also been reviewed recently [44].

CNTs can be effectively suspended and solubilized in Nafion (a perfluorosulfonated polymer) to modify the electrode surfaces for the development of an electrochemical CH₄ sensor. So far there are two major types of CNTs: the multi-walled carbon nanotubes (MWCNTs) and the single-walled carbon nanotubes. MWCNTs are outstanding catalyst support, attributing to its excellent mechanical property, nanometer size and very large surface area [43,45].

Although a variety of modified electrodes have been studied, to our knowledge, the use of MWCNTs–Nafion nickel hydroxide modified nickel (NMN) electrode for CH₄ determination has not been reported. This paper reports the enhanced electrochemical reactivity of CH₄ at a MWCNTs–Nafion NMN electrode at ambient conditions based on the superior catalytic properties of

* Corresponding author. Tel.: +86 351 7018613; fax: +86 351 7018613.

** Corresponding author. Tel.: +852 3411 7839; fax: +852 3411 7348.

E-mail addresses: dc@sxu.edu.cn (C. Dong), mfchoi@hkbu.edu.hk (M.M.F. Choi).

Ni(OH)₂/NiOOH and the fast electron transfer properties of MWCNTs. The objective of this work is to develop a rapid and sensitive electrochemical method for determination of CH₄.

2. Experimental

2.1. Chemicals and reagents

Nafion 117 (5%, w/v in alcoholic solution) was purchased from Aldrich–Sigma and was diluted to 0.1% (w/v) Nafion with ethanol before use. High purity nitrogen (99.99%, v/v) and oxygen (99.99%, v/v) gases and standard CH₄ gases (1.0, 1.5, 3.0, 5.0, 10.0, 16.0, and 99.9%, v/v) balanced with N₂ were purchased from Fujiang Special Gas Company (Taiyuan, China). All reagents of analytical grades or above were used as received without further purification. All aqueous solutions were prepared with doubly distilled water. MWCNTs (purity ≥90%) were obtained from Keer Instruments Co., Ltd. (Shenzhen, China).

2.2. Apparatus

All the electrochemical experiments were performed with CHI660C electrochemical workstation (CH Instruments, Shanghai, China) using a conventional three-electrode cell. The working electrode was a modified Ni electrode (2 mm diameter, Lanlike Instruments, Tientsin, China). An Ag/AgCl electrode (Model CHI 111P, CH Instruments) and a platinum wire were used as reference and auxiliary electrodes, respectively. The electrodes were inserted into a 50-mL electrochemical cell (Model CHI 222, CH Instruments) for electrochemical measurements at ambient conditions.

The infrared (IR) spectrum of the treated MWCNTs was acquired on a Perkin Elmer Paragon 700 Fourier transform IR spectrometer (Waltham, MA, USA). The transmission electron microscopic (TEM) images were performed on a JEM-100CX transmission electron microscope (Japan Electronic Company, Tokyo, Japan).

2.3. Preparation of nickel hydroxide modified nickel electrode

The Ni working electrode was polished with 0.03 μm alumina powders on a micro-cloth and then thoroughly cleansed ultrasonically with ethanol and doubly distilled water, respectively. The clean Ni electrode was positioned in a 50-mL electrochemical cell containing 25 mL of 1.0 M NaOH. Cyclic voltammetric (CV) scan (0.00–0.60 V) at a scan rate of 100 mV/s was applied to the Ni electrode. After 300 cycles, a nickel hydroxide layer was formed on the Ni electrode surface.

2.4. Preparation of MWCNTs–Nafion nickel hydroxide modified nickel electrode

0.5 g pristine MWCNTs were dispersed in 60 mL of concentrated HNO₃ and refluxed for 6 h at 110 °C [46]. It is well-known that this treatment causes segmentation and carboxylation of MWCNTs at their terminus. The IR spectrum of the treated MWCNTs was used to confirm the presence of CO- (H) group on the surfaces of MWCNTs (peaks at 1105 and 1568 cm⁻¹). MWCNTs/Nafion suspension was prepared by adding 1.0 mg of the acid-treated MWCNTs in 5.0 mL of 0.1% (w/v) Nafion ethanol solution and then sonicated in a sonicator for 20 min. 11.0 μL of MWCNTs–Nafion suspension was dropped on the NMN electrode surface and left at ambient conditions to evaporate the ethanol. Another MWCNTs–Nafion Ni electrode without Ni(OH)₂ was also fabricated in the same manner for comparison. The morphology of MWCNTs–Nafion and MWCNTs–Nafion/Ni(OH)₂ films was studied by TEM. Since the modified electrodes could not be inserted directly into the TEM, only the surface layers of MWCNTs–Nafion

and MWCNTs–Nafion/Ni(OH)₂ were removed from their respective Ni electrode and dropped on carbon-coated copper grids for TEM imaging.

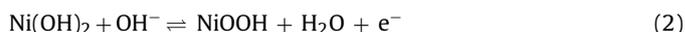
2.5. Electrochemical measurement

Various concentrations of standard CH₄ gases were passed through the electrochemical cell with 1.0 M NaOH as the supporting electrolyte for 15 min. CV was then applied to study the electrochemical behavior of the dissolved CH₄. Differential pulse voltammetry (DPV) was employed to investigate the relationship of the CH₄ oxidation peak current and CH₄ concentration. All electrochemical experiments were conducted at ambient conditions.

3. Results and discussion

3.1. Preparation of nickel hydroxide modified nickel electrode

Fig. 1 presents 300 consecutive CV scans of a Ni electrode in 1.0 M NaOH solution at a scan rate of 100 mV/s. In the first cycle, a pair of broad redox peak potentials appeared at 348 and 458 mV (vs. Ag/AgCl) that are assigned to the Ni(II)/Ni(III) redox couple [40]. In the second cycle, the redox peak potentials shifted to 328 and 423 mV, respectively. A shoulder also developed on the cathodic peak at about 256 mV. Upon further cycling, the currents increased gradually but the peak potentials did not change much. Eventually only one pair of redox peaks was observed. The changes in the shapes and positions of the peaks are probably due to changes in the crystal structures of nickel hydroxide and nickel oxy-hydroxide of the electrochemically formed surface film [47]. It has been reported that the electro-oxidation of Ni electrode involves firstly the formation of α-Ni(OH)₂ which is slowly converted to β-Ni(OH)₂ and then finally partially to oxy-hydroxide [48,49]. Both the electrodeposited nickel hydroxide and nickel oxy-hydroxide phases are believed to be non-stoichiometric [50,51]. The formation of nickel hydroxide and nickel oxy-hydroxide on the nickel electrode surface can be expressed by the following mechanisms:



Since nickel hydroxide (Ni(OH)₂) and nickel oxy-hydroxide (NiOOH) can easily form on the surface of a Ni electrode in 1.0 M

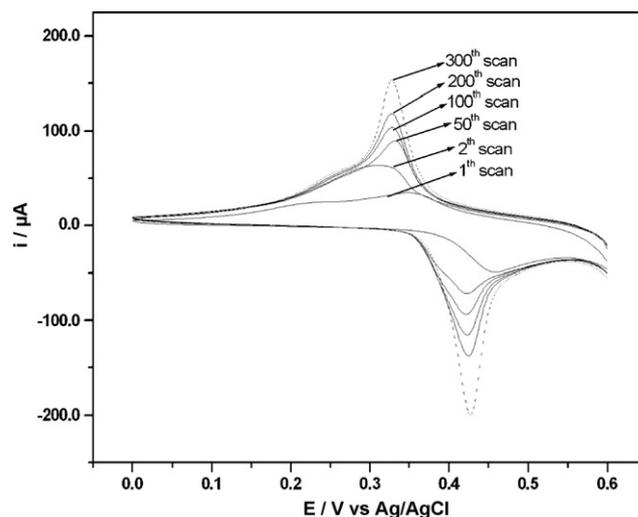


Fig. 1. Cyclic voltammograms of nickel electrode in 1.0 M NaOH at the scan rate of 100 mV/s.

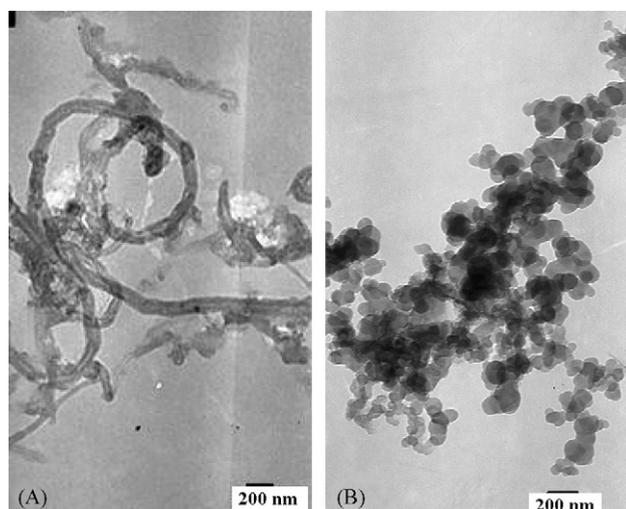


Fig. 2. TEM images of (A) MWCNTs–Nafion and (B) MWCNTs–Nafion/Ni(OH)₂ films.

NaOH by applying many cycles of CV, they are promising electrocatalysts for the oxidization of CH₄ (*vide infra*).

3.2. Morphology of MWCNTs–Nafion and MWCNTs–Nafion/Ni(OH)₂ films

Fig. 2 depicts the TEM images of MWCNTs–Nafion and MWCNTs–Nafion/Ni(OH)₂ films. Fig. 2(A) shows that the acid-treated MWCNTs have outer diameters of 40–80 nm and tube lengths of several micrometers. They are entangled because of their large surface area and the van der Waals attraction. On the other hand, Fig. 2(B) displays that the nickel hydroxide clusters agglomerate and attach densely on the surface of MWCNTs which can then be employed for further electrochemical experiments.

3.3. Electrochemical behavior of methane on nickel hydroxide modified nickel electrode

In our preliminary work, CVs of CH₄ at NMN electrode in various concentrations of NaOH were investigated. It was found that 1.0 M NaOH produced the highest CH₄ oxidation peak current. Therefore, 1.0 M NaOH solution was selected as the optimal electrolyte for subsequent work. Fig. 3 displays the CVs of air, N₂ and CH₄ in 1.0 M NaOH solutions at NMN, MWCNTs/NMN, and MWCNTs–Nafion/NMN electrodes, respectively. It is observed that the redox currents and potentials are almost the same for all the modified electrodes with air and N₂, indicating that O₂ did not significantly interfere the electrochemical behavior of the modified electrodes. Fig. 3(A) depicts the CVs of NMN electrode in the absence and presence of CH₄. The anodic current increased while the cathodic current decreased slightly in the presence of CH₄. The slight increase in the anodic current is perhaps attributed to the oxidization of CH₄ and its oxidation may be mediated by the high valence nickel species on the Ni surface electrode. Much higher anodic and cathodic currents were recorded for the MWCNTs/NMN electrode (Fig. 3(B)) as compared to the NMN electrode (Fig. 3(A)) in the presence of air, N₂, or CH₄. The increase in current is possibly attributed to the unique structure and extraordinary electron transfer promotion properties of MWCNTs at the electrode surface. In addition, the MWCNTs/NMN electrode produced larger anodic current with CH₄ than air and N₂. It is possible that CH₄ was electrocatalytically oxidized at the MWCNTs/NMN surface. The increase in anodic peak current for CH₄ is more profound at the MWCNTs/NMN electrode than the NMN electrode. These results indicate that the oxidation current of CH₄ can be increased by adding MWCNTs to

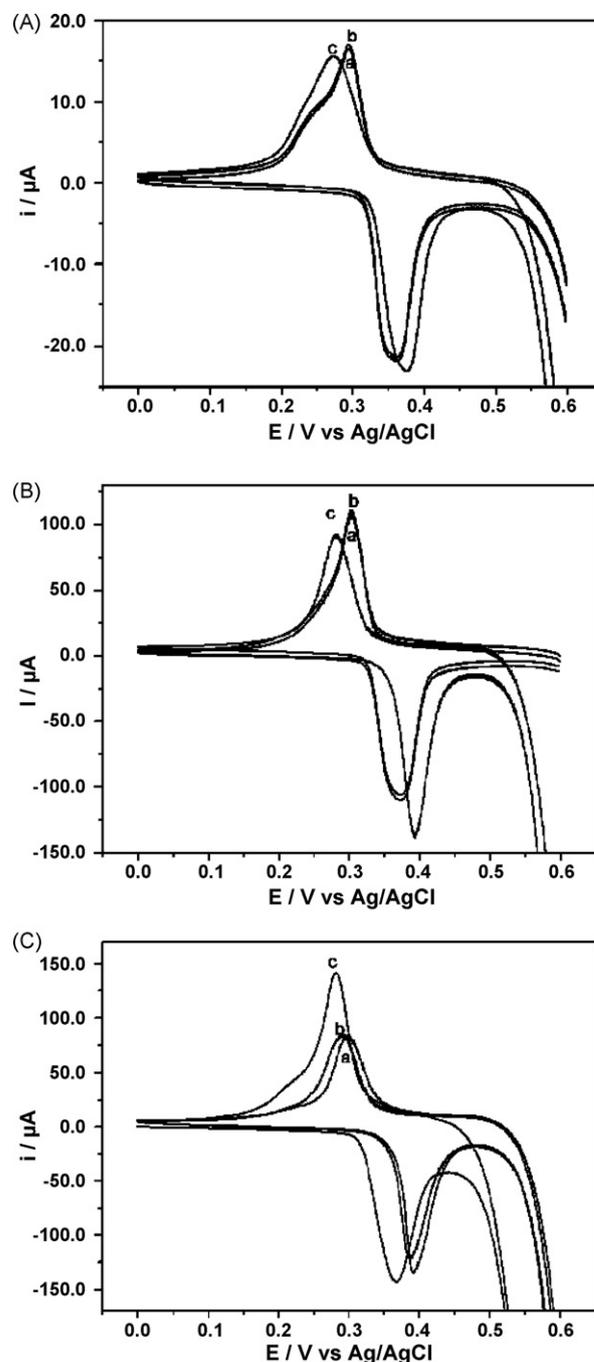


Fig. 3. Cyclic voltammograms of (a) air, (b) N₂ and (c) CH₄ (99.9%, v/v) in 1.0 M NaOH at (A) NMN, (B) MWCNTs/NMN and (C) MWCNTs–Nafion/NMN electrodes. The scan rate was 20 mV/s.

NMN electrode. However, the slight shifting of the anodic peak to higher potential is still not clearly understood.

It has been reported that Nafion is a useful perfluorosulfonated polymer which can prevent electro-catalyst from leaching and interference from other substances. As such, Nafion was added to the MWCNTs/NMN electrode to further improve its electrochemical properties. Fig. 3(C) displays the CVs of the MWCNTs–Nafion/NMN electrode in 1.0 M NaOH solutions saturated with air, N₂ and CH₄. The magnitudes of the cathodic and anodic currents were more or less the same as that of MWCNTs/NMN electrode but the CH₄ oxidation peak current increases more significantly and the peak potential is positively shifted as depicted in Fig. 3(C)(c). The enhancement in the peak current is strongly attributed to the subtle

electronic properties and larger surface areas of MWCNTs as well as the lipophilic backbone structure of Nafion. Nafion is able to mix with MWCNTs/Ni(OH)₂ and form a network on the Ni electrode. Thus, the response of the MWCNTs–Nafion/NMN electrode in 1.0 M NaOH to CH₄ was further investigated (*vide infra*).

3.4. Optimization of fabrication of MWCNTs–Nafion/NMN electrode

The response current of the MWCNTs–Nafion/NMN electrode to CH₄ is largely affected by the amount of MWCNTs, the concentration of Nafion and the volume of MWCNTs–Nafion suspension used for fabrication of MWCNTs–Nafion/NMN electrode. As such, these factors were investigated in detail by CV. First, different concentrations of Nafion from 0.05 to 0.3% (w/v) at a 0.05% (w/v) interval were prepared with 0.20 mg/mL of MWCNTs. Then these MWCNTs–Nafion/NMN electrodes were subject to CV study in the presence of CH₄ (not shown). At lower concentrations of Nafion ($\leq 0.05\%$, w/v), the MWCNTs–Nafion film was not stable and came off easily from the NMN electrode. At higher concentrations of Nafion ($>0.1\%$, w/v), thicker films were formed which slowed down the mass transfer of CH₄ to the NMN electrode, and thus greatly reduced the anodic current signals. The optimal concentration of Nafion which produced the highest signal to CH₄ was 0.1% (w/v).

Second, different concentrations of MWCNTs from 0.10 to 0.50 mg/mL were prepared with 0.1% (w/v) Nafion. The current response was proportional to the MWCNTs concentration up to 0.20 mg/mL and began to decline above 0.20 mg/mL (not shown). Thus, the optimal concentration of MWCNTs was chosen as 0.20 mg/mL.

Third, the volume of MWCNTs–Nafion solution for coating on NMN electrode was investigated. Fig. 4 displays the CH₄ peak current against the volume of MWCNTs–Nafion solution used for fabrication of MWCNTs–Nafion/NMN electrode. The peak current increased gradually with the increase in MWCNTs–Nafion solution from 0.0 to 11.0 μL . The increase in loading of MWCNTs and Nafion onto the NMN electrode surface provides more active sites for CH₄ accumulation and thus increases the oxidation current proportionally. The peak current leveled off at 12.0 μL and further increase in loading of MWCNTs–Nafion solution caused the peak current to decline. This is because the MWCNTs–Nafion film became too thick and thus slowed down the mass transport and charge transfer rate.

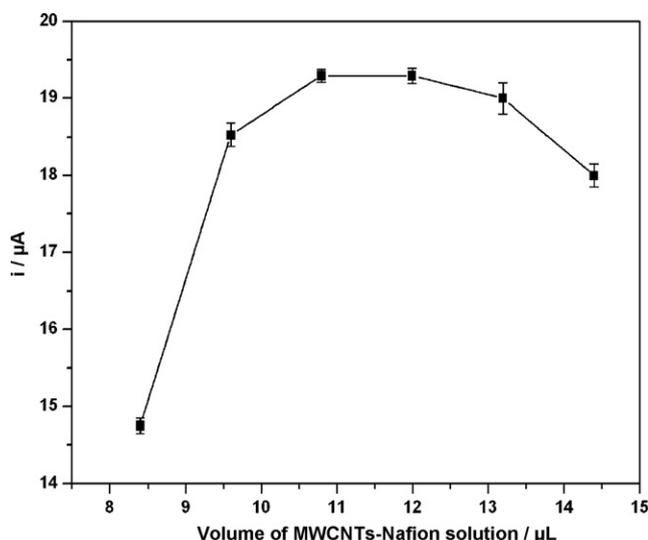


Fig. 4. Plot of methane peak current as a function of the volume of MWCNTs–Nafion solution used for fabrication of MWCNTs–Nafion/NMN electrode.

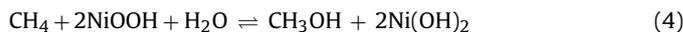
In summary, the optimal concentrations of Nafion and MWCNTs for fabricating MWCNTs–Nafion/NMN electrode were 0.1% (w/v) and 0.20 mg/mL, respectively and the volume of MWCNTs–Nafion suspension was 11.0 μL .

3.5. Electrochemical properties of methane on MWCNTs–Nafion/NMN electrode

In order to investigate the rate-determining step of CH₄ oxidation at MWCNTs–Nafion/NMN electrode, the effect of scan rate on the CV peak current was studied in 1.0 M NaOH. If the adsorbed species is electrochemically active and adsorption-controlled, the peak current will increase linearly with the scan rate as represented by the following equation [52]:

$$I_p = \frac{QnFv}{4RT} \quad (3)$$

where I_p is the peak current, Q is the reductive peak area, n is the number of electron transferred in the reaction, v is the scan rate, F is the Faraday constant, R is the molar gas constant, and T is the temperature. Fig. 5 displays the CVs of CH₄ (99.9%) on MWCNTs–Nafion/NMN electrode at different scan rates. The peak current is directly proportional to the scan rate (inset of Fig. 5), indicating that the electrochemical reaction of CH₄ on MWCNTs–Nafion/NMN electrode is an adsorption-control process. The number of electron transferred in the reaction n was calculated to be about 2 according to the slope of Eq. (3) and inset of Fig. 5, inferring that a two-electron transfer took place in the reaction. The total anodic oxidation of CH₄ is postulated as reaction (4):



In brief, CH₄ can be efficiently oxidized to CH₃OH by the electrocatalyst NiOOH in 1.0 M NaOH.

3.6. Measurement of methane on the MWCNTs–Nafion/NMN electrode

The response of MWCNTs–Nafion/NMN electrode to various concentrations of CH₄ in 1.0 M NaOH was investigated. DPV technique was applied to the electrochemical cell as it is more sensitive than the CV method. Fig. 6 depicts the DPVs of

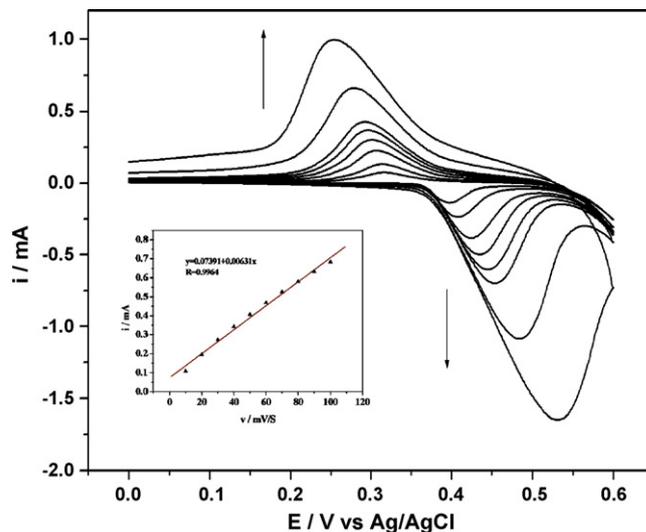


Fig. 5. Cyclic voltammograms of MWCNTs–Nafion/NMN electrode in 1.0 M NaOH saturated with methane (99.9%, v/v) at various scan rates of 10–100 mV/s. The inset displays the linear plot of the anodic peak current and the CV scan rate.

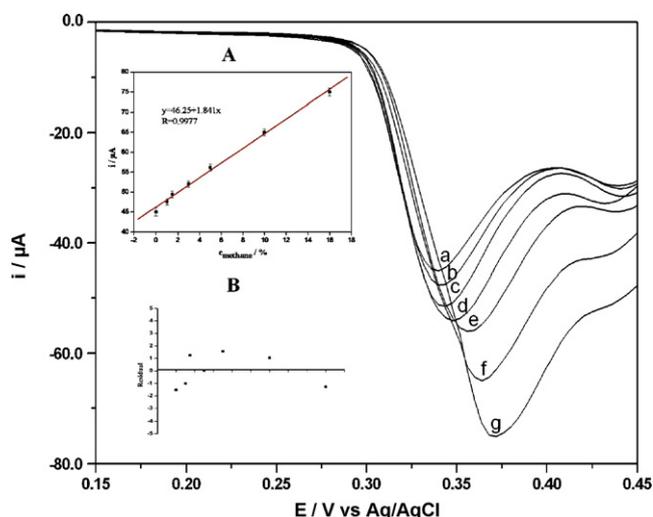


Fig. 6. Differential pulse voltammograms of MWCNTs–Nafion/NMN electrode in 1.0 M NaOH saturated with various concentrations of (a) 0.0%, (b) 1.0%, (c) 1.5%, (d) 3.0%, (e) 5.0%, (f) 10.0%, and (g) 16.0% (v/v) methane. Each data point was obtained from five replicate measurements. Inset (A) shows the linear calibration plot of the peak current against the concentration of methane. Inset (B) displays the residual plot of the calibration curve in inset (A).

MWCNTs–Nafion/NMN electrode in 1.0 M NaOH saturated with various concentrations of CH₄. The anodic peak current is linearly related to the CH₄ concentration in the range of 0.0–16.0% (v/v). The linear regression equation is: $i = 1.841 C_{\text{methane}} + 46.25$ with the correlation coefficient of 0.9977 (inset (A) of Fig. 6), where i is the anodic peak current (μA) and C_{methane} is the concentration of CH₄ (% v/v) passing through the electrolyte. The residual plot of the calibration curve depicted in the inset (B) of Fig. 6 shows that the data points are roughly and randomly distributed above and below the calibration curve. The relative standard deviation for 3.0% (v/v) CH₄ is 1.80% ($n = 5$).

3.7. Interferences

The interferences of gases were also evaluated. In real situations, N₂ and O₂ are the potential interferences in the analysis of CH₄. It was found that N₂ and O₂ did not cause any interference to the detection of CH₄.

4. Conclusion

In summary, we have described a method for fabrication of MWCNTs–Nafion/NMN electrode and determination of CH₄ at ambient conditions. The Ni electrode modified surface exhibited better electro-catalytic activity to CH₄ oxidation due to the electro-catalytic property of high valence nickel species and the subtle electronic properties and larger surface area of MWCNTs–Nafion. The CH₄ reaction on the MWCNTs–Nafion/NMN electrode was an adsorption-control process. A linear relationship between the oxidation current and CH₄ concentration was obtained. Our work offers a novel method to determine CH₄ in aqueous electrolyte at ambient conditions. In addition, it is anticipated that it can be further modified to detect CH₄ directly in air. This work is currently in progress in our laboratory.

Acknowledgments

This work is supported by the Key Project of National Natural Science Foundation of China (50534100) and the Shanxi Province Graduate Student Innovative Plan (07010700).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.snb.2009.02.065.

References

- [1] O. Hugon, M. Sauvan, P. Benech, C. Pijolat, F. Lefebvre, Gas separation with a zeolite filter, application to the selectivity enhancement of chemical sensors, *Sens. Actuators B* 67 (2000) 235–243.
- [2] K. Ohta, H. Terai, I. Kimura, K. Tanaka, Simultaneous determination of hydrogen, methane, and carbon monoxide in water by gas chromatography with a semiconductor detector, *Anal. Chem.* 71 (1999) 2697–2699.
- [3] W. Janicki, W. Chrzanowski, P. Zwan, J. Namiesnik, Automated analyser for monitoring the contents of hydrocarbons in gas emitted from exploratory bore-holes in the gas and oil industry, *J. Autom. Method Manage.* 25 (2003) 141–147.
- [4] T.L. Hansen, J.E. Schmidt, I. Angelidaki, E. Marca, J.L. Jansen, H. Mosbaek, T.H. Christensen, Method for determination of methane potentials of solid organic waste, *Waste Manage.* 24 (2004) 393–400.
- [5] M.T. Roberge, J.W. Finley, H.C. Lukaski, A.J. Borgerding, Pulsed discharge detector: theory and applications, *J. Chromatogr. A* 1027 (2004) 63–68.
- [6] C. Maris, M.Y. Chung, R. Lueb, U. Kirschke, R. Meller, M.J. Fox, A.W. Ho, F. Kramp, S.E. Paulson, Development of instrumentation for simultaneous analysis of total non-methane organic carbon and volatile organic compounds in ambient air, *Atmos. Environ.* 37 (2003) S149–158.
- [7] A. Raksit, S. Johri, Determination of dissolved volatile hydrocarbons in environmental aqueous samples by headspace-gas chromatography with flame ionization detection, *Am. Lab.* 35 (2003) 10–13.
- [8] M. Kaminski, R. Kartanowicz, D. Jastrzebski, M.M. Kaminski, Determination of carbon monoxide, methane and carbon dioxide in refinery hydrogen gases and air by gas chromatography, *J. Chromatogr. A* 989 (2003) 277–283.
- [9] D.E.J. Worthy, I. Levin, N.B.A. Trivett, A.J. Kuhlmann, J.F. Hopper, M.K. Ernst, Seven years of continuous methane observations at a remote boreal site in Ontario, Canada, *J. Geophys. Res.* 103 (1998) 15995–16007.
- [10] T. Seiyama, A. Kato, K. Fujiishi, M. Nagatani, A new detector for gaseous components using semiconductive thin films, *Anal. Chem.* 34 (1962) 1502–1503.
- [11] M. Fleischer, S. Kornely, T. Weh, J. Frank, H. Meixner, Selective gas detection with high-temperature operated metal oxides using catalytic filters, *Sens. Actuators B* 69 (2000) 205–210.
- [12] G. Faglia, E. Comini, G. Sberveglieri, R. Rella, P. Siciliano, L. Vasanelli, Square and collinear four probe array and Hall measurements on metal oxide thin film gas sensors, *Sens. Actuators B* 53 (1998) 69–75.
- [13] M. Benounis, N. Jaffrezic-Renault, J.P. Dutasta, K. Cherif, A. Abdelghani, Study of a new evanescent wave optical fibre sensor for methane detection based on cryptophane molecules, *Sens. Actuators B* 107 (2005) 32–39.
- [14] G. Tournier, C. Pijolat, Influence of oxygen concentration in the carrier gas on the response of tin dioxide sensor under hydrogen and methane, *Sens. Actuators B* 61 (1999) 43–50.
- [15] E. Llobet, J. Orts, X. Vilanova, J. Brezmes, X. Correig, Selective methane detection under varying moisture conditions using static and dynamic sensor signals, *Sens. Actuators B* 60 (1999) 106–117.
- [16] C. Pijolat, C. Pupier, M. Sauvan, G. Tournier, R. Lalauze, Gas detection for automotive pollution control, *Sens. Actuators B* 59 (1999) 195–202.
- [17] F. Quaranta, R. Rella, P. Siciliano, S. Capone, M. Epifani, L. Vasanelli, A. Licciulli, A. Zocco, A novel gas sensor based on SnO₂ thin film for the detection of methane at low temperature, *Sens. Actuators B* 58 (1999) 350–355.
- [18] B.W. Licznarski, K. Nitsch, H. Tetrycz, P.M. Sześciowka, K. Wisniewski, Humidity insensitive thick film methane sensor based on SnO₂/Pt, *Sens. Actuators B* 57 (1999) 192–196.
- [19] W. Schmid, N. Barsan, U. Weimar, Sensing of hydrocarbons with tin oxide sensors: possible reaction path as revealed by consumption measurements, *Sens. Actuators B* 89 (2003) 232–236.
- [20] L. Gajdošik, The derivation of the electrical conductance/concentration dependency for SnO₂ gas sensor for ethanol, *Sens. Actuators B* 81 (2002) 347–350.
- [21] M. Saha, A. Banerjee, A.K. Halder, J. Mondal, A. Sen, H.S. Maiti, Effect of alumina addition on methane sensitivity of tin dioxide thick films, *Sens. Actuators B* 79 (2001) 192–195.
- [22] E. Llobet, J. Rubio, X. Vilanova, J. Brezmes, X. Correig, J.W. Gardner, E.L. Hines, Electronic nose simulation tool centred on Spice, *Sens. Actuators B* 76 (2001) 419–429.
- [23] O. Hammerichin, H. Lund, O. Hammerich (Eds.), *Organic Electrochemistry*, 4th ed., Marcel Dekker, NY, 2000.
- [24] D.B. Clark, M. Fleischmann, D. Pletcher, The partial anodic oxidation of aliphatic hydrocarbons in aprotic solvents, *J. Electroanal. Chem.* 42 (1973) 133–138.
- [25] D.H. Geske, Electrooxidation of tropilidene to tropylium ion, *J. Am. Chem. Soc.* 81 (1959) 4145–4147.
- [26] P.G. Gassman, R. Yamaguchi, Electron transfer from highly strained polycyclic molecules, *Tetrahedron* 38 (1982) 1113–1122.
- [27] M. Fleischmann, D. Pletcher, The electrochemical oxidation of some aliphatic hydrocarbons in acetonitrile, *Tetrahedron Lett.* (1968) 6255–6258.
- [28] J. Bertram, M. Fleischmann, D. Pletcher, The anodic oxidation of alkanes in fluoro-sulphonic acid; a novel synthesis of α,β -unsaturated ketones, *Tetrahedron Lett.* (1971) 349–350.

- [29] P.L. Fabre, J. Devynck, B. Tremillon, The anodic oxidation of alkanes in anhydrous hydrogen fluoride and related superacid media, *Tetrahedron* 38 (1982) 2697–2701.
- [30] T. Otagawa, S. Zaromb, J.R. Stetter, Electrochemical oxidation of methane in nonaqueous electrolytes at room temperature: application to gas sensors, *J. Electrochem. Soc.* 132 (1985) 2951–2957.
- [31] T. Otagawa, S. Zaromb, J.R. Stetter, Transient response of electrochemical biosensors with asymmetrical sandwich membranes, *Sens. Actuators B* (1985) 65–71.
- [32] L.W. Niedrach, Galvanostatic and volumetric studies of hydrocarbons adsorbed on fuel cell anodes, *J. Electrochem. Soc.* 111 (1964) 1309–1317.
- [33] H. Binder, A. Kohling, H. Krupp, K. Richter, G. Sanderstede, Electrochemical oxidation of certain hydrocarbons and carbon monoxide in dilute sulfuric acid, *J. Electrochem. Soc.* 112 (1965) 355–359.
- [34] A.H. Taylor, S.B. Brummer, The adsorption and oxidation of hydrocarbons on noble metal electrodes. VII. Oxidative adsorption of methane on platinum electrodes, *J. Phys. Chem.* 72 (1968) 2856–2860.
- [35] P. Jacquinet, B. Muller, B. Wehrli, P.C. Hauser, Determination of methane and other small hydrocarbons with a platinum–Nafion electrode by stripping voltammetry, *Anal. Chim. Acta* 432 (2001) 1–10.
- [36] M.G. Susteric, R.O. Cordova, W.E. Triaca, A.J. Arvia, The electrosorption of methane and its potentiodynamic electrooxidation on platinumized platinum, *J. Electrochem. Soc.* 127 (1980) 1242–1248.
- [37] Y. Lu, J. Li, J. Han, H.T. Ng, C. Binder, C. Partridge, M. Meyyappan, Room temperature methane detection using palladium loaded single-walled carbon nanotube sensors, *Chem. Phys. Lett.* 391 (2004) 344–348.
- [38] L.R. Damgaard, N.P. Revsbech, A microscale biosensor for methane containing methanotrophic bacteria and an internal oxygen reservoir, *Anal. Chem.* 69 (1997) 2262–2267.
- [39] L.R. Damgaard, N.P. Revsbech, W. Reichardt, Use of an oxygen-insensitive microscale biosensor for methane to measure methane concentration profiles in a rice paddy, *Appl. Environ. Microb.* 64 (1998) 864–870.
- [40] M. Jafarian, M.G. Mahjani, H. Heli, F. Gopal, M. Heydarpoor, Electrocatalytic oxidation of methane at nickel hydroxide modified nickel electrode in alkaline solution, *Electrochem. Commun.* 5 (2003) 184–186.
- [41] L.J. Sheli, Helical microtubules of graphitic carbon, *Nature* 354 (1991) 56–58.
- [42] P.M. Ajayan, Nanotubes from carbon, *Chem. Rev.* 99 (1999) 1787–1800.
- [43] J.M. Nugent, K.S.V. Santhanam, A. Rubio, P.M. Ajayan, Fast electron transfer kinetics on multiwalled carbon nanotube microbundle electrodes, *Nano Lett.* 1 (2001) 87–91.
- [44] Q. Zhao, Z. Gan, Q.K. Zhuang, Electrochemical sensors based on carbon nanotubes, *Electroanalysis* 14 (2002) 1609–1613.
- [45] L.J. Sheli, Single-shell carbon nanotubes of 1-nm diameter, *Nature* 363 (1993) 603–605.
- [46] S.C. Tsang, Y.K. Chen, P.J.F. Harris, M.L.H. Green, A simple chemical method of opening and filling carbon nanotubes, *Nature* 372 (1994) 159–162.
- [47] A.A. El-Shafei, Electrocatalytic oxidation of methanol at a nickel hydroxide: glassy carbon modified electrode in alkaline medium, *J. Electroanal. Chem.* 471 (1999) 89–95.
- [48] G.W.D. Briggs, P.R. Snodin, Ageing and the diffusion process at the nickel hydroxide electrode, *Electrochim. Acta* 27 (1982) 565–569.
- [49] F. Hahn, B. Beden, M.J. Croissant, C. Lamy, In situ UV-visible reflectance spectroscopic investigation of the nickel electrode-alkaline solution interface, *Electrochim. Acta* 31 (1986) 335–342.
- [50] J. Desilvestro, D.A. Corrigan, M.J. Weaver, Characterization of redox states of nickel hydroxide film electrodes by in situ surface Raman spectroscopy, *J. Electrochem. Soc.* 135 (1988) 885–892.
- [51] R. Barnard, C.F. Randell, Studies concerning charged nickel hydroxide electrodes. VII. Influence of alkali concentration on anodic peak positions, *J. Appl. Electrochem.* 13 (1983) 89–95.
- [52] A.J. Bard, L.R. Faulkner, *Electrochemical Methods, Fundamentals and Application*, Wiley, New York, 1980.

Biographies



Jie Qiao is an instructor in Shanxi Medical University. She received her BSc degree in applied chemistry and MSc degree in analytical chemistry in 1997 and 2002 from Shanxi University, respectively. Her doctorate research is in analytical chemistry under the supervision of professors Chuan Dong and Shaomin Shuang. She has been working in the electro-property of methane at modified nickel electrode. Her research interest is the development of electrochemical sensors based on carbon nanotubes. She is an instructor of chemistry, Shanxi medical University, Shanxi, China. BS of Shanxi University, 1997; MS of Shanxi University in Application chemistry, 2002. Currently she is working towards the PhD degree at Shanxi University of analytical chemistry. Her interests are electro-analytical chemistry, flow injection method of analysis and electrochemical sensors.

Shengnan Tang received her BSc degree in applied chemistry in 2007 from Shanxi University. She is currently pursuing her MSc degree at Tongji University under the supervision of professor Tonghua Li. Her research focuses on the proteomic profiles of prostate cancer cells of mouse.

Yanni Tian received her BSc degree in analytical chemistry and MSc degree in inorganic chemistry in 1982 and 1991 from Shanxi University, respectively, and PhD degree in 1996 from Nanjing University. She is a professor at Shanxi University. Her current research interest is biological electrochemistry.

Shaomin Shuang received her BSc degree in chemistry and MSc degree in analytical chemistry in 1986 and 1989 from Shanxi University, respectively, and PhD degree in 1998 from South China University of Technology. She has been a professor at Shanxi University since 2002. Her current research interests include biochemical analysis and supramolecular chemistry.

Chuan Dong received his BSc degree in chemistry and MSc degree in analytical chemistry in 1984 and 1990, respectively, and PhD degree in 2002 from Shanxi University. His research interests are chemosensor and environmental analytical chemistry.

Martin M.F. Choi received his BSc degree in applied chemistry in 1990 from Hong Kong Baptist University, and MSc degree and PhD degree in analytical chemistry in 1992 and 1994, respectively, from Bristol University and University of the West of England, Bristol. He has been an associate professor at Hong Kong Baptist University since 2001. His current research interests include biosensor, HPLC and CE separation of metal nanoparticles, and environmental analysis and monitoring.