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

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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 (CH$_4$) 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 CH$_4$ 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 ($i_p$) and CH$_4$ concentration ($C_{methane}$) was obtained: $i_p = 1.841 C_{methane} + 46.25$, where $i_p$ 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) CH$_4$ was 1.80% ($n = 5$). The proposed Ni modified electrode is anticipated to provide a promising technique to detect CH$_4$ at ambient conditions.

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1. Introduction

Methane (CH$_4$) is a major component of the widely used natural fuel gas in industry and private households. It can be released from the walls of coal mines. Explosion will occur when its concentration in air reaches to 5–16% (v/v). Therefore the monitoring of CH$_4$ 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, CH$_4$ is relatively difficult to detect at ambient conditions as its chemical reactivity is low. The commonly used techniques for CH$_4$ 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 CH$_4$ 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 CH$_4$ at ambient conditions, electrode materials of transition metals such as nickel (Ni) or Ni alloys have to be used in strong alkaline 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 CH$_4$ 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 CH$_4$ 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 CH$_4$ 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 CH$_4$ determination has not been reported. This paper reports the enhanced electrochemical reactivity of CH$_4$ at a MWCNTs–Nafion NMN electrode at ambient conditions based on the superior catalytic properties of...
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 CH$_4$.

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 CH$_4$ gases (1.0, 1.5, 3.0, 5.0, 10.0, 16.0, and 99.9%, v/v) balanced with N$_2$ were purchased from Fujian 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 $\geq$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 $\mu$m 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 HNO$_3$ and refluxed for 6 h at 110 $^\circ$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 mL 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 CH$_4$ 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 CH$_4$. Differential pulse voltammetry (DPV) was employed to investigate the relationship of the CH$_4$ oxidation peak current and CH$_4$ 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 Ni$_2$O$_3$–Ni(OH)$_2$ which is slowly converted to Ni$_2$O$_3$ 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:

\[
\text{Ni} + 2\text{OH}^- \rightarrow \text{Ni(OH)}_2 + 2\text{e}^- \quad (1)
\]

\[
\text{Ni(OH)}_2 + \text{OH}^- \rightarrow \text{NiOOH} + \text{H}_2\text{O} + \text{e}^- \quad (2)
\]

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 NaOH solution, the fast electron transfer properties of MWCNTs are studied.
NaOH by applying many cycles of CV, they are promising electro-catalysts for the oxidation of CH$_4$ (*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 CH$_4$ at NMN electrode in various concentrations of NaOH were investigated. It was found that 1.0 M NaOH produced the highest CH$_4$ 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, N$_2$, and CH$_4$ 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 N$_2$, indicating that O$_2$ 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 CH$_4$. The anodic current increased while the cathodic current decreased slightly in the presence of CH$_4$. The slight increase in the anodic current is perhaps attributed to the oxidation of CH$_4$ 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, N$_2$, or CH$_4$. 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 CH$_4$ than air and N$_2$. It is possible that CH$_4$ was electro-catalytically oxidized at the MWCNTs/NMN surface. The increase in anodic peak current for CH$_4$ is more profound at the MWCNTs/NMN electrode than the NMN electrode. These results indicate that the oxidation current of CH$_4$ can be increased by adding MWCNTs to 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, N$_2$, and CH$_4$. The magnitudes of the cathodic and anodic currents were more or less the same as that of MWCNTs/NMN electrode but the CH$_4$ 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 (≤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.

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]:

\[
I_p = \frac{QnF\nu}{4RT}
\]

where \(I_p\) is the peak current, \(Q\) is the reductive peak area, \(n\) is the number of electron transferred in the reaction, \(\nu\) 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):

\[
\text{CH}_4 + 2\text{NiOOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{OH} + 2\text{Ni(OH)}_2
\]

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

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**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.

**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.
MWCNTs–Nafion/NMN electrode and determination of CH₄.

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 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 (µmol/L) 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).

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


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