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SHORT COMMUNICATION

Electrooxidation of ethanol on carbon nanotubes–nickel nanoparticles composites in alkaline media

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Abstract In this report, the preparation of carbon nanotubes–Ni nanoparticles composites (CNT–Ni) is presented. The morphology and elemental composition of CNT–Ni composites were examined by transmission electron microscopy and X-ray diffraction. The electrochemical behaviour of carbon nanotubes–Ni nanoparticles composites in an aqueous solutions of alkali and alkaline solutions of ethanol has been studied by linear sweep voltammetry. The peak on the potentiodynamic curve for CNT–Ni composite electrode in alkaline solutions of ethanol is observed which is ascribed to the ethanol oxidation in alkaline medium. The results obtained are discussed from the point of view of employment of the CNT–Ni composites for the catalytic electrodes of fuel cells.

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Introduction

Carbon nanotubes (CNTs) due to their nanometre size and unique chemical and physical properties attract the interest of numerous researchers for many applications—for example, batteries [1], storage of hydrogen [2], chemical sensors [3], energy storage devices [4], etc. These materials are also considered to be potential supports for heterogeneous catalysts. The use of carbon nanotubes as a support for catalytic materials is the promising method to prepare novel highly efficient electrodes for fuel cells. Good properties of the catalyst support, such as high surface area, low resistance and high stability, are essential for catalytic electrodes.

Direct alcohol fuel cells based on liquid fuels such as methanol and ethanol have attracted enormous attention. Pt-based nanoparticles dispersed on materials with high surface area are commonly used for the electrooxidation of liquid fuels [5, 6]. However, it is well established that nickel can also be used as a catalyst for oxidation of organic compounds including methanol [7] and ethanol [8].

On the basis of the above statement, a CNT and Ni composite are expected to be a promising new catalyst material. The CNT–Ni composites are usually produced by electrodeposition [9, 10], electroless deposition [11] or pyrolisis [12, 13].

In the present study, the synthesis of carbon nanotubes–nickel nanoparticles composites, structure and elemental composition of such kind of composites and the investigations of catalytic properties of CNT–Ni composite are presented.

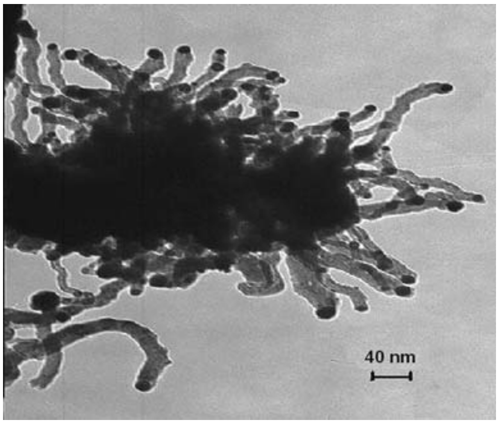


Fig. 1 TEM image of the CNT–Ni composites

Materials and methods

Carbon nanotubes were grown at 420–450 °C by means of catalytic pyrolysis of granular polyethylene in helium atmosphere using a Ni plate as a substrate [12]. Various methods of promotion of nickel surface substrates were used: abrasive grinding and mechanical and chemical polishing [14]. It allowed the obtainment of nanocomposite materials consisting mainly of carbon nanotubes and Ni nanoparticles at their tips.

The obtained composites were examined by transmission electron microscopy (TEM) and X-ray diffraction (DRON-3M, CuKα).

The electrocatalytic properties of CNT–Ni composites were investigated by linear sweep voltammetry. An Ecotest-VA potentiostat was employed for linear sweep voltammetry measurements. Voltammetric experiments were carried out in a three-electrode system at room temperature. Carbon nanotubes–Ni nanoparticles composite electrodes (geometry area 0.2 cm^2) were used as working electrodes. A platinum foil and saturated Ag–AgCl served as counter and reference electrode, respectively. Three kinds of electrolytes 0.1 M KOH, 0.1 M KOH+0.1 M C2H5OH, 0.1 M KOH+ 0.2 M C2H5OH were used. These solutions were prepared using high pure chemicals and distilled water.

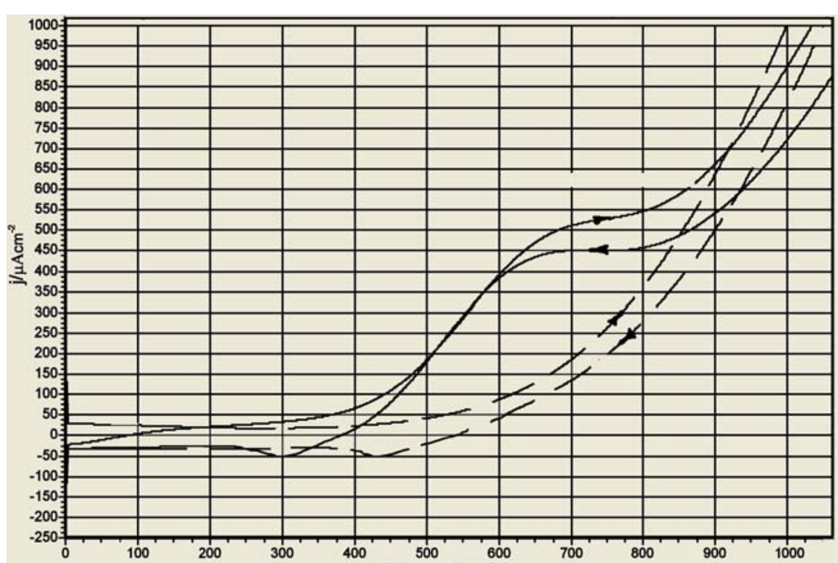
Results and discussion

The morphology of the CNT–Ni electrodes is shown in Fig. 1. From observation in many experiments; along with nanotubes, the nanofibres are found the range of carbon nanotube and nanofibre diametres is about 40 nm, a great deal of metallic nanoparticles are with size of 10–40 nm. The X-ray diffraction pattern of CNT–Ni composites are similar to those observed by E.F. Kukovitsky et al. [14].

The electrochemical activity of CNT–Ni composite electrodes was measured in aqueous solutions of alkali and alkaline solutions of ethanol. The results obtained exhibit high catalytic activity of CNT–Ni composites in the above-mentioned solutions. The linear sweep voltammogrammes of CNT–Ni composite electrode in the aqueous solution of alkali and alkaline solution of ethanol are presented in Fig. 2. By comparing with the voltammogramme in the absence of alcohol, an alcohol oxidation peak can be clearly observed in the voltammogramme on CNT–Ni electrode in the presence of ethanol.

In the oxidation of alcohols at the nickel electrode in alkaline solution, different hypotheses are given in litera-

Fig. 2 The linear sweep voltammogrammes of CNT–Ni electrode in 0.1 M KOH+0.2 M C2H5OH (*solid line*) and in 0.1 M KOH. Linear sweep rate 20 mV s^{-1}



ture. Fleishmann et al. [15] suggested that the organic species are oxidised by the mechanism:

$$Ni(OH)_2 \rightarrow NiO(OH) + e^- + H^+;$$
$$Ni(OH) + \text{organic compound} \rightarrow Ni(OH)_2 + \text{product.}$$

El-Shafei [16] examined methanol oxidation on a nickel–glassy carbon composite electrode. The results reported led to the conclusion that methanol is oxidised with the participation of Ni3 + species. Rahim et al. [17] studied the methanol oxidation on nickel–graphite electrode and made the same conclusion. Skowronsky and Wazny [18] have shown that methanol oxidation takes place on a nickel foam electrode via NiO(OH) layer which is formed on the electrode surface. On the other hand, Taraszewska and Roslonek [19] proposed that methanol molecules penetrated the nickel hydroxide film and were oxidised by the OH ions trapped in the film.

Ethanol reveals much complicated oxidation scheme with a great number of possible intermediates and much less is known about the course of the oxidation process. We suggest that oxidation of ethanol on CNT–Ni electrode in alkaline media undergoes the reversible transformation of Ni(OH)2–NiO(OH) and then NiO(OH) acts as an electrocatalyst.

Conclusions

Composites of carbon nanotubes and nickel nanoparticles were prepared. The morphology and elemental composition of such composite materials were examined by TEM and X-ray diffraction. Most catalytically grown nanotubes contained small particles of nickel at their tips. The electrocatalytic properties of CNT–Ni composite were investigated in various solutions by linear sweep voltammetry. The study reveals that the foregoing composites show a high electrocatalytic activity towards the ethanol oxidation in alkaline media and may be of great interest in direct alcohol fuel cells.

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