CARBON NANOTUBES AS A CATALYTIC SUPPORT FOR THE METHANOL OXIDATION

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Introduction

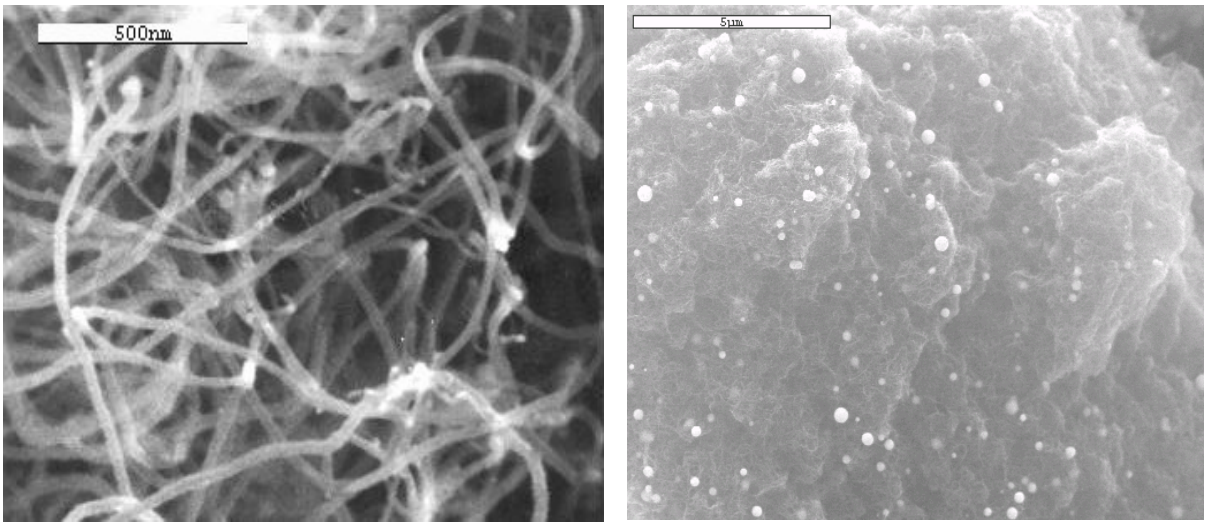
Fuel cells based on the direct oxidation of methanol (DMFC) represent an attractive storage system due to the high theoretical energy (6 kWh/kg), low cost of methanol and environmental friendly final products (CO_2 and H_2O). Since, methanol oxidation in acidic medium requires the application of noble metals, an intensive research is devoted for finding cheaper catalysts. To decrease the cost of catalyst as well as enhance its selectivity, a significant attention is paid for the usage of two component alloys. Methanol oxidation in acidic medium has been tested using such metals as ruthenium, platinum, tin and their binary alloys [1-2]. The catalytic effect of metallic particles strongly depends on the preparation method but also on the support used.
Carbon nanotubes (CNTs) have been used as a novel support of highly dispersed catalysts [3-5]. Due to their unusual electrical, microtextural and mechanical properties as well as open mesoporous network they are an attractive support for the direct oxidation of methanol. In this paper, potential application of supported bimetallic alloys will be shown.

Experimental

Two types of multiwalled carbon nanotubes were tested as a catalyst support: CNTs obtained by the decomposition of acetylene at 600^0C on a $Co_xMg_{(1-x)}O$ solid state solution [6] and CNTs from the decomposition of propylene at 800^0C using an alumina template. Platinum, ruthenium and Pt-Ru alloys were used as a catalyst for methanol oxidation. The catalytic particles were deposited galvanostatically in acidic medium. The electrolytic solutions were composed of 0.01 mol.L^{-1} $RuCl_3 \cdot xH_2O$ and/or 0.01 mol.L^{-1} H_2PtCl_6. For comparison carbon fibrous material made from polyacrylonitrile has been also used as a support. The dispersion of the catalyst particles was studied by SEM (Hitashi S 4200) and TEM (Philips CM20). Methanol oxidation was investigated in aqueous acidic medium (1 mol.L^{-1} CH_3OH + 1 mol.L^{-1} H_2SO_4) by voltammetry method at a scan rate of 5 mV/s and galvanostatic discharging (AUTOLAB-ECOCHEMIE). The counter electrode was from platinum whereas the reference electrode was the mercury/mercurous sulfate system (Hg/Hg_2SO_4).

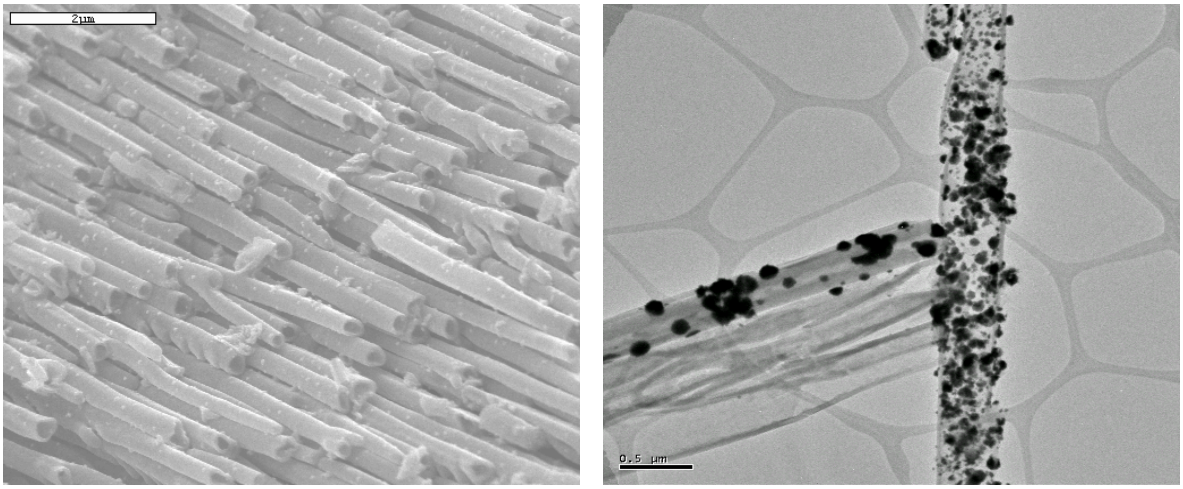
Results and Discussion

Different types of carbon nanotubes/catalyst composite with Pt, Ru, Pt-Ru were observed by SEM and TEM and characterized by EDX analysis. Examples of catalytic and template CNTs without catalyst and with electrodeposited Pt-Ru particles are shown in Fig. 1 and 2. Although the particle size of the catalyst clusters presents a high dispersion, a few nm particles could be easily found.



(a) (b)

Figure 1. SEM images of (a) CNTs alone; (b) CNTs with Pt-Ru particles



(a) (b)

Figure 2. (a) SEM (b) TEM image of template CNTs with electrodeposited Pt-Ru particles

The CNTs/catalyst composites were tested for the methanol oxidation reaction in 1mol.L^{-1} H_2SO_4. The voltammetry experiments allow to estimate the methanol oxidation current for the Pt catalyst (Fig. 3) and Pt-Ru alloy (Fig. 4). The most characteristic feature is a very useful shift of the oxidation peak to a more negative value in the case of the Pt-Ru alloy and also a decrease of the rest potential from – 0.184 V to – 0.34 V vs Hg/Hg_2SO_4.

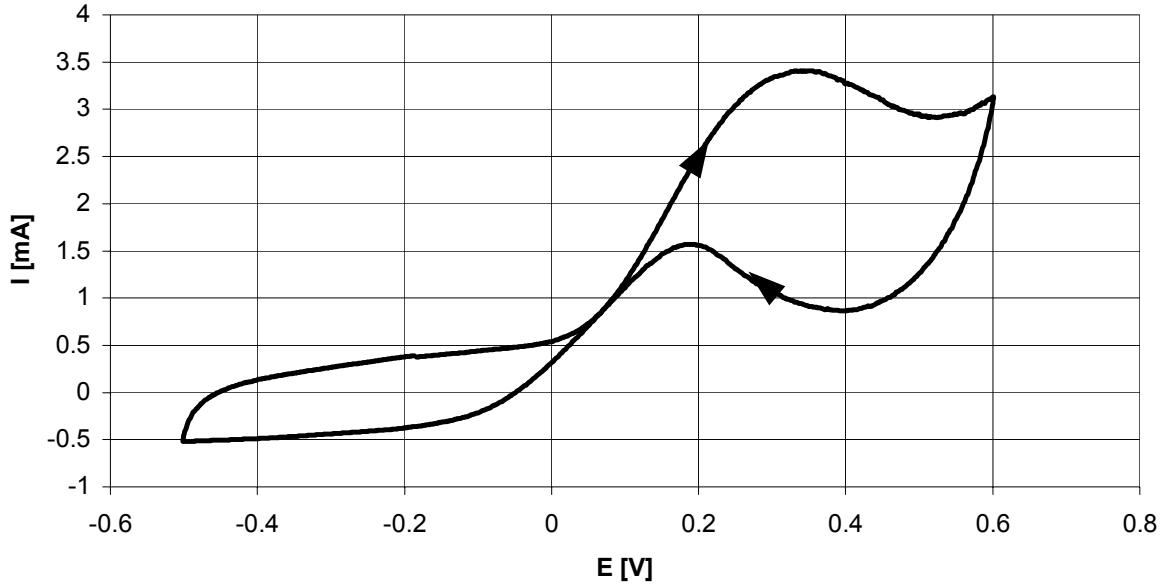


Figure 3. Voltammetry characteristics of methanol oxidation (1 mol.L^{-1}) in sulfuric acid (1 mol.L^{-1}) on carbon nanotubes with Pt particles.

The high electrocatalytic activity of metallic particles supported on CNTs can be also explained by specific interaction between catalyst and CNTs. It was already proved that the electrode processes in the presence of CNTs proceed with a higher charge transfer due to the peculiar CNTs electronic structure.
Different combinations of catalysts (single components and binary alloys) supported on CNTs and PAN fabric have been tested using various current regimes from 0.01 A/g to 0.5 A/g. From the galvanostatic experiments, even one order of magnitude higher current load could be reached for the nanotubular supported catalyst in comparison to catalysts based on polyacrylonitrile carbon supports.
Trials were also undertaken for investigation of polymer electrolyte based on ion-exchange hydrated perfluorosulfonic Nafion® membrane. Performance of methanol oxidation was moderately better if Nafion® membrane was used.

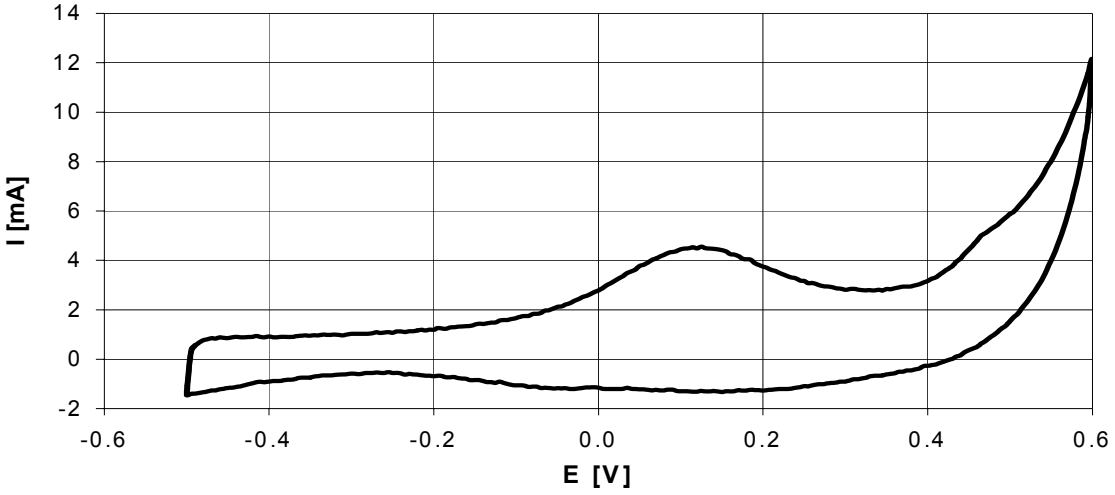


Figure 4. Voltammetry characteristics (5 mV/s) of methanol oxidation (1 mol.L^{-1}) in sulfuric acid (1 mol.L^{-1}) on Pt-Ru catalytic particles electrodeposited on CNTs.

Conclusions

It was clearly shown that the better results of methanol oxidation are obtained for carbon materials with electrodeposited Pt-Ru particles in comparison with the performance of the single metallic components. Due to the presence of open mesopores, the CNTs material loaded by catalyst fulfils perfectly the conditions of good conductivity and accessibility by the reagents. Such a support allows an easy diffusion of methanol and reaction products. High currents of methanol oxidation of 380 –500 mA/g have been found for the Pt-Ru electrodeposited particles.

References

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