



J. Serb. Chem. Soc. 75 (10) 1435–1439 (2010)
JSCS–4065

EXTENDED ABSTRACT

The electrochemical properties of carbon nanotubes and carbon XC-72R and their application as Pt supports*

MAJA D. OBRADOVIĆ

*Institute of Chemistry, Technology and Metallurgy, University of Belgrade,
Njegoševa 12, 11000 Belgrade, Serbia*

(Received 20 May 2010)

Abstract: The results of an investigation of two samples of commercial multi-walled carbon nanotubes and a sample of carbon black, in the raw and activated state, were presented in the lecture. The activation of the carbon materials led to the formation of an abundance of oxygen-containing functional groups on the surface, an increased electrochemically active surface area, an enhanced charge storage ability and a promotion of the electron-transfer kinetics. It was presented that the morphology of the carbon nanotubes is important for the electrochemical properties, because nanotubes with a higher proportion of edge and defect sites showed faster electron transfer and pseudocapacitive redox kinetics. Modification of oxidized nanotubes by ethylenediamine and wrapping by poly(diallyldimethylammonium chloride) led to a decrease in the electrochemically active surface area and to reduced electron-transfer kinetics. Pt nanoparticles prepared by the microwave-assisted polyol method were deposited at the investigated carbon materials. A much higher efficiency of Pt deposition was observed on the modified CNTs than on the activated CNTs. The activity of the synthesized catalyst toward electrochemical oxygen reduction was almost the same as the activity of the commercial Pt/XC-72 catalyst.

Keywords: carbon nanotubes; morphology; electrochemical properties; Pt nanoparticles; electrocatalyst for oxygen reduction.

Carbon nanotubes (CNTs) have attracted enormous attention because of their unique structure, excellent chemical and thermal stability, mechanical properties and, in some cases, even metallic conductivity.^{1,2} The tubular structure of carbon

obradovic@ihtm.bg.ac.rs

Serbian Chemical Society member.

* Lecture at the Meeting of the Electrochemical Section of the Serbian Chemical Society, held 2 February, 2010.

doi: 10.2298/JSC100520081O

nanotubes makes them unique among different forms of carbon and they have proven themselves as extremely promising nanostructured materials for electrochemical application, such as catalysis,³ chemical sensing,^{4,5} and gas and energy storage.⁶ The structure of the carbon material can play an important role in the dispersion of a catalyst, in its crystallographic characteristics and, consequently, in its electrochemical properties.^{7,8}

In this lecture, a survey of the results of an investigation of the physicochemical and electrochemical properties of two types of commercial carbon nanotubes (Sigma-Aldrich and Sun Nanotech) and carbon black (Vulcan XC-72R), in the raw and acid-activated state, was presented. The carbon powders were activated by treating the samples with concentrated $\text{H}_2\text{SO}_4 + \text{HNO}_3$ in an ultrasonic bath. Changes in the chemical composition of the carbon surfaces upon activation were investigated by Fourier transform infrared spectroscopy and the Boehm titration method.^{9–11} The results indicated that the groups formed on the surface were dominantly acid groups. The stability of water suspensions of the carbon powders before and after activation was investigated by UV–visible spectroscopy and it was registered that an abundance of oxygen-containing functional groups made the carbon surfaces more hydrophilic. The structural characterization of the carbon nanotubes, performed by atomic force microscopy, indicated that activated Sigma-Aldrich nanotubes were straight with the corrugated walls (bamboo-like structure), while the Sun Nanotech nanotubes are tortuous with smooth walls.

The influence of activation and morphology on the electrochemical properties of the carbon powders, applied on a gold substrate in the form of a thin-film, was investigated by cyclic voltammetry and electrochemical impedance spectroscopy in 0.10 M H_2SO_4 and in 1.0 M KCl. The steady-state capacitive potentiodynamic curves of the raw CNT feature a rectangular-shaped profile with a rather low specific capacitance. After activation, the capacitance increased and a pair of broad peaks appeared at around 0.6 V, which is commonly attributed to surface oxidation/reduction processes of the hydroquinone/quinone groups.^{1,12,13}

The electron-transfer properties of the investigated carbons were probed by the simple redox transition of the $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ couple in 1.0 M KCl + 5.0 mM $\text{K}_4[\text{Fe}(\text{CN})_6]$. The voltammograms of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ on the thin films of raw carbons show rather low currents with not well resolved redox peaks, while the activated carbons show an almost reversible currents transition superposed on high capacitance currents. The currents for the straight CNTs with corrugated walls were the highest and the peak separation was the closest to that of reversible kinetics. The results of a detailed interpretation of the EIS measurements were consistent with the properties of the carbons established by cyclic voltammetry. It was concluded that the nanotubes with the higher proportion of edge and defect sites were the most active for electron transfer processes, when compared to XC and tortuous nanotubes with smooth walls.

Modification of the CNTs with covalently attached ethylenediamine (eda)⁸ and poly(diallyldimethylammonium chloride) (polymer), adsorbed on the surface of the nanotubes by electrostatic interaction¹⁴ led to a certain agglomeration of the CNTs, a decrease in the capacitance of the material, and a reduced rate of electron transfer between the nanotubes and solution species. Addition of a nitrogen heteroatom to active carbon was used to form an electrode material with intermediate acid–base properties.¹⁵ An investigation of the $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ redox process on CNTs modified with diethylenetriamine, triethylenetetramine and 1,6-hexanediamine¹¹ indicated even more hindered electron transfer than on eda-CNT.⁸

A colloidal Pt solution was prepared in a microwave oven from H_2PtCl_6 with ethylene glycol as the reducing agent⁷ and the Pt nanoparticles were supported on the investigated carbons. The Pt content was determined by thermogravimetric analysis of the deposited Pt/C in an oxygen atmosphere. The deposition of Pt nanoparticles on the oxidized CNTs resulted in a Pt/CNTs material with a very low Pt content. However, modification of oxidized CNTs with either eda or the polymer prior to mixing with the colloidal Pt solution increased the amount of deposited Pt. The much higher efficiency of Pt deposition on the modified CNTs than on the oxidized CNTs was ascribed to a decrease of the negative charge on the surface of the CNTs that was formed by dissociation of acidic oxygen-containing groups. An investigation by transmission electron microscopy (TEM) revealed that the mean diameter of Pt particles in Pt/eda-CNT was 2.5 ± 0.5 nm and that their distribution on the support was homogenous with no evidence of pronounced agglomeration of the particles.

The electrochemical properties of the synthesized catalyst were investigated in 0.10 M H_2SO_4 by using cyclic voltammetry and compared to the results obtained with the commercial Pt/XC-72 catalyst manufactured by E-TEK. The real Pt surface was determined from the desorption charge of underpotentially deposited hydrogen. The polarization curves for oxygen reduction on all the investigated catalysts almost overlapped. The Tafel plots exhibited two distinct linear regions with a slope of $-2.3RT/F$ in the low current densities region and $-2.3 \times 2RT/F$ in the high current densities region, which are the same as those observed on polycrystalline Pt and Pt/C catalyst in acidic solution.¹⁶ Although noble metal catalysts supported on CNTs were found to be more active for methanol oxidation than catalysts supported on other high area carbons,⁷ a recent study¹⁷ and the present results showed that the carbon support has no influence on the activity of the electrocatalysts for oxygen reduction.

Acknowledgements. The results presented in the lecture were obtained with the financial support of the Ministry of Science and Technological Development of the Republic of Serbia, Projects No. 142048 and 142056.

ИЗВОД

ЕЛЕКТРОХЕМИЈСКЕ КАРАКТЕРИСТИКЕ УГЉЕНИЧНИХ НАНОЦЕВИ И УГЉЕНИКА
XC-72R И ЊИХОВА ПРИМЕНА У СИНТЕЗИ Pt КАТАЛИЗАТОРА

МАЈА Д. ОБРАДОВИЋ

*Институт за хемију, технологију и металургију, Универзитет у Београду,
Ђевошева 12, 11000 Београд, Србија*

У оквиру предавања су приказани резултати испитивања две врсте комерцијалних вишеслојних угљеничних наноцеви и узорка угљеничног праха развијене површине пре и након активације хемијском оксидацијом. Оксидација узорака доводи до израженог формирања кисеоничних група на површини угљеничних материјала, повећања електрохемијски активне површине као и до убрзања преноса наелектрисања. Показано је да морфологија угљеничних наноцеви има значајан утицај на њихове електрохемијске карактеристике. Узорак са већим уделом ивица и дефеката показао је бржу кинетику преноса наелектрисања и већу псеудокапацитивност. Модификовање оксидованих наноцеви етилендиамином и полимером поли(диалилдиметиламонијум-хлоридом) доводи до смањења активне површине и до споријег преноса наелектрисања. Наночестице платине, синтетисане у раствору етиленгликола у микроталасној пећници, нанете су на испитиване угљеничне материјале. Количина нанете Pt је много већа на модификованим него на оксидованим наноцевима. Активност синтетисаних узорака за електрохемијску редукцију кисеоника је упоређена са активношћу комерцијалног катализатора Pt/XC-72 за исту реакцију и показало се да су њихове специфичне активности приближно једнаке.

(Примљено 20. маја 2010)

REFERENCES

1. J. J. Gooding, *Electrochim. Acta* **50** (2005) 3049
2. S. N. Marinković, *J. Serb. Chem. Soc.* **73** (2008) 891
3. K. Kinoshita, *Carbon, Electrochemical and Physicochemical Properties*, Wiley, New York, 1987
4. H. Tang, J. Chen, K. Cui, L. Nie, Y. Kuang, S. Yao, *J. Electroanal. Chem.* **587** (2006) 269
5. H. Yaghoobian, H. Karimi-Maleh, M. Ali Khalilzadeh, F. Karimi, *J. Serb. Chem. Soc.* **74** (2009) 1443
6. B. E. Conway, *Electrochemical Supercapacitors*, Kluwer Academic/Plenum Publishing, New York, 1999
7. X. Li, W. X. Chen, J. Zhao, W. Xing, Z. D. Xu, *Carbon* **43** (2005) 2168
8. G. D. Vuković, M. D. Obradović, A. D. Marinković, J. R. Rogan, P. S. Uskoković, V. R. Radmilović, S. L. Gojković, *Mater. Chem. Phys.*, submitted for publication
9. H. P. Boehm, *Carbon* **32** (1994) 759
10. M. D. Obradović, G. D. Vuković, S. I. Stevanović, V. V. Panić, P. S. Uskoković, A. Kowal, S. L. Gojković, *J. Electroanal. Chem.* **634** (2009) 22
11. G. Vuković, A. Marinković, M. Obradović, V. Radmilović, M. Čolić, R. Aleksić, P. S. Uskoković, *Appl. Surf. Sci.* **255** (2009) 8067
12. H. A. Andreas, B. E. Conway, *Electrochim. Acta* **51** (2006) 6510
13. E. Fuente, J. A. Menéndez, D. Suárez, M. A. Montes-Morán, *Langmuir* **19** (2003) 3505
14. K. Jiang, A. Eitan, L. S. Schandler, P. M. Ajayan, R. W. Siegel, N. Grobert, M. Mayne, M. Reyes-Reyes, H. Terrones, M. Terrones, *Nano Lett.* **3** (2003) 275

15. S. C. Roy, A. W. Harding, A. E. Russell, K. M. Thomas, *J. Electrochem. Soc.* **144** (1997) 2323
16. N. R. Elezović, B. M. Babić, N. V. Krstajić, S. L. Gojković, L. M. Vračar, *J. Serb. Chem. Soc.* **73** (2008) 641
17. E. K. Tuseeva, N. A. Mayorova, V. E. Sosenkin, N. F. Nikol'skaya, Y. M. Vol'fkovich, A. V. Krestinin, G. I. Zvereva, V. A. Grinberg, O. A. Khazova, *Russ. J. Electrochem.* **44** (2008) 884.