ISSN 1023-1935, Russian Journal of Electrochemistry, 2016, Vol. 52, No. 10, pp. 955–959. © Pleiades Publishing, Ltd., 2016.
Published in Russian in Elektrokhimiya, 2016, Vol. 52, No. 10, pp. 1073–1078.

Comparison of Different Carbon Nanostructures Influence on Potentiometric Performance of Carbon Paste Electrode[1]

Fatemeh Honarasa[a, *], **Maryam Zare**[a], **and Saeed Yousefinejad**[b, **]
[a] *Department of Chemistry, Shiraz Branch, Islamic Azad University, Shiraz, Iran*
[b] *Department of Occupational Health Engineering, School of Health, Shiraz University of Medical Sciences, Shiraz, Iran*
**e-mail: fhonarasa@gmail.com, honarasa@iaushiraz.ac.ir*
***e-mail: yousefinejad.s@gmail.com, yousefisa@sums.ac.ir*

Received October 2, 2015

Abstract—Recently, different carbon nanomaterials were introduced for construction of electrochemical sensors. In this study, the influence of carbon nanomaterial on performance of carbon paste potentiometric electrode was investigated. In this manner, different kinds of carbon nanomaterial, i.e., graphene, graphene oxide and carbon nanotube (CNT) were used as a conduction phase in carbon paste electrode. Then, potentiometric characteristics of the corresponding paste electrodes such as calibration slope, linear range, detection limit, response time and stability were compared with each other. The results appeared comprehensive findings about the role of electrode's content in electrochemical performance.

Keywords: carbon paste electrode, potentiometry, carbon nanotube, graphene, graphene oxide

DOI: 10.1134/S1023193516100050

INTRODUCTION

After discovery of carbon paste electrodes (CPE) by Adams in 1958, this category of electrodes were utilized extensively in many electrochemical disciplines [1, 2]. The widespread application of CPEs is due to its advantages over other kinds of working electrodes. Some of these advantages are ease of preparation, low cost, new surface without affection of prehistory of electrode, small residual current, low ohmic resistance and no risk of mechanical damage of the electrode surface [2, 3]. As a result, more than 2000 articles were published after about half of century of its discovery for many applications because CPEs were used in conjugation with various electrochemical techniques for different applications [2]. One of these applications is in potentiometric sensors either in titration manner or direct mode [2, 4, 5]. In the latter, carbon paste electrodes have been used as ion selective electrodes. In comparison with ion-selective electrodes based on polymeric membranes, the CPEs offer a benefits such as chemical inertness, robustness, low cost, renewability, stable response, low ohmic resistance, no need for internal solution and suitability for a variety of sensing and detection applications [6].

Unmodified CPE is consisting of two main phases; conductive and binder phases. The performance of CPEs significantly depends on the properties of these two phases [4, 7] which can make an impression on selectivity of the corresponding electrode. The properties of any CPE reflect the nature (chemical and physical) of binder, and utilized carbon material as well [8]. It is noteworthy that conductivity is the main characteristics of an electrochemical sensor. Non-conductive mineral oils are traditional binders to prevent carbon paste from dissolution in aqueous media. In the last decade, the use of other conductive binders such as ionic liquids were also examined in construction of new generations of CPEs [6, 9]. It was shown that increasing the conductivity of CPE by exchanging the non-conductive binder with conductive ones can improve the performance of CPE.

On the other hand, undoubtedly the carbon materials are the main component in the CPEs. Traditionally, spectroscopic graphite with particles in the low micrometric scale (typically, 5–20 μm) was used as the conductive phase [2]. Smaller particle size of graphite material produces smooth texture and favorable mechanical and electrochemical properties [4]. It is well-known that different types of carbon materials can give different characteristics and electrochemical performances [3, 10].

In recent years, carbon nanomaterials have attracted great attention in construction of sensors due to their significant advantages such as their small size and good electrochemical properties over other types of carbon materials [11, 12]. Two main carbonaceous nanomaterials which attracted enormous interest in electrochemistry are carbon nanotube (CNT) and

---

[1] The article is published in the original.

graphene. CNT is one-dimensional allotrope of carbon which has several important properties including remarkable electrical, chemical, mechanical and structural properties [11, 13–15]. Carbon nanotube-based electrodes have ability to mediate electron-transfer reactions with an electro active species in solution [16]. Also, they can enhance the electrochemical reactivity of important biomolecules [17]. CNT has acted as efficient ion to electron transducer in potentiometric analysis [18]. Graphene is another nanostructure of carbon which is known as two-dimensional material. Graphene has been attracted a lot of attention due to its unique physicochemical properties such as high surface area, excellent conductivity, high mechanical strength, and ease of functionalization and mass production [12]. Graphene-based electrodes has shown good macroscopic scale conductivity [19, 20] and also wonderful electrocatalytic activity [20, 21]. These two carbonaceous nanostructures i.e., CNT and graphene have similar composition and also have similar properties. The chemical bonding of these nanostructures are composed entirely of sp^2 bonds. Both of them have been utilized as the first choices in construction of high-speed sensors due to their high electron mobility along their structures [18]. Also, both nanomaterials have large number of carbon atoms on their surfaces.

The main focus in this study is comparison the performance of CNT and graphene as two well-known carbon allotropes in construction of carbon based potentiometric sensors. For better comparison, graphene oxide, which is the precursor of the synthesis of graphene, was also applied for construction of CPE. The results can be used to have estimation about selection of the kind of carbon material in construction of carbon paste potentiometric based sensors. This work can be helpful for better design of cation selective electrodes.

EXPERIMENTAL

Chemicals and Apparatus

All reagents were of analytical reagent grade. Double distilled water was used throughout. The graphite powder was obtained from Fluka. Multi-walled carbon nanotube (diam. × length 110–170 nm × 5–9 μm) from Aldrich and paraffin oil from Merck were purchased. Graphene was synthesized as described elsewhere [22, 23]. Firstly, graphite oxide was synthesized from graphite by the Hummers method [22]. Then, reduction of graphene oxide was carried out by hydrazine to synthesize graphene [23]. Stock solutions (0.1, 0.01 and 0.001 M) of each cation were prepared freshly by using of corresponding salts (Merck).

The electromotive force (EMF) measurements were performed with EDT GP353 pH-meter. A two electrode cell configuration was used with carbon paste electrode as the indicator electrode and a double junction Ag/AgCl electrode (Metrohm) as a reference electrode.

Preparation of Carbon Paste Electrodes

The carbon paste was prepared by hand mixing of each allotropes of carbon including graphite, graphene, graphene oxide and multi-walled carbon nanotube with paraffin oil. Ratio of carbon allotrope to the paraffin oil in all pastes was 70:30%. The resulting pastes were packed into the Teflon tube and the electrical contact was provided by a stainless steel handle. It should be noted that the electrode surface was polished on a weighing paper to give a fresh surface before each experiment.

RESULTS AND DISCUSSION

Based on previous reports, unmodified carbon paste electrode shows potentiometric response toward six cations namely Ag(I), Cu(II), Hg(II), Al(III), Cr(III) and Fe(III) [6, 24]. To elucidate the influence of kinds of nanostructure material on potentiometric response of carbon paste electrode, several experiments were performed for all four carbon paste electrodes, i.e., graphite, graphene, graphene oxide and carbon nanotube paste electrodes. In this way, some analytical figures of merit including slope of calibration curve, linear range, limit of detection (LOD) and response time for four constructed carbon paste electrodes toward six mentioned cations were obtained. In this way, better comparison between all types of carbonaceous material can be made. Then, responses of carbon paste electrodes were compared with each other.

Comparison of Nernstian Behavior

In potentiometry, the first important parameter for indicator electrodes is the slope of calibration curve. Clearly, the best slopes are Nernstian ones. So, the calibration curves of all six cations at different carbon paste electrodes were obtained. For all cases, the calibration curves were repeated three times and results were summarized in Table 1. Obviously, all four carbon paste electrodes show potentiometric response toward six cations. But the responses of all four electrodes are different. The differences in all carbon paste electrodes are due to the difference in properties of utilized carbon-allotrope such as conductivity, lipophilicity or presence of oxide groups and surface area. Also, it should be emphasized that the effective and corresponding parameter depends on the nature of target cation. The goal of this study is showing such difference in comparing the response of various analytes.

For almost cases, replacement of carbon nanostructure instead of graphite in CPE results in higher calibration curve slope (super-Nernstian response) which is due to the more homogeneity of resulting

Table 1. Slopes and squares of corresponding correlation coefficients (R^2) for calibration curves of carbon paste electrodes with different carbon nanostructures

	Slope ± standard deviation (R^2)					
	Ag^+	Cu^{2+}	Hg^{2+}	Fe^{3+}	Cr^{3+}	Al^{3+}
Graphite	59.1 ± 2.3 (0.993)	28.2 ± 2.3 (0.987)	129.2 ± 16.4 (0.987)	29.7 ± 5.1 (0.989)	108.1 ± 1.9 (0.994)	25.3 ± 5.1 (0.979)
CNT	65.1 ± 3.8 (0.993)	30.8 ± 3.3 (0.992)	125.8 ± 4.9 (0.993)	27.8 ± 6.2 (0.967)	92.0 ± 3.6 (0.990)	87.3 ± 7.5 (0.987)
Graphene oxide	65.0 ± 1.9 (0.990)	41.0 ± 4.2 (0.995)	125.9 ± 5.1 (0.984)	34.2 ± 1.8 (0.990)	25.2 ± 3.3 (0.986)	165.9 ± 3.9 (0.986)
Graphene	62.3 ± 0.9 (0.992)	35.0 ± 2.4 (0.992)	184.2 ± 2.2 (0.926)	104.9 ± 23.4 (0.983)	64.8 ± 3.2 (0.993)	105.8 ± 4.0 (0.988)

pastes. Carbon nanostructures due to low particle size can make a more homogeneous paste rather than micro sized graphite. In fact, the presence of nanostructures in the corresponding pastes leads uniform distribution of the particles. Typical morphology of heterogeneous carbon pastes, which is responsible for almost each property of the resultant carbon paste electrodes, can be classified as a solid dispersion system (dispersion of carbone structures in paraffin medium) [2]. So, by using nanostructures (graphene and carbon nanotubes) instead of graphite, as a conductive phase, more dispersive system can be obtained. Our experimental results showed that potentiometric response of corresponding graphene and carbon nanotube paste were altered in compare with graphite based electrode and caused an increase in the slope of response plot. Based on previous reports, a super-Nernstian response is usually caused by an inward flux of primary ions into the electrode surface [25]. So, it seems that at almost all utilized carbon-allotrope paste electrodes, cations prefer to transfer into the electrode surface which leads to a super-Nernstian behavior. Response of traditional CPE to some cations is incurred by paraffin liquid extraction and by the exchange current caused by some cations on the surface of the carbon [6]. So there are three main parameters which affected on the potentiometric response of CPE, (i) lipophilicity/presence of oxide groups at the electrode surface, (ii) conductivity of resulting paste and (iii) surface area of conductive phase. Another point is homogeneity of prepared paste, because decreasing the size of utilized carbon material can lead to more homogeneous paste. All above-mentioned parameters can affect the potentiometric response of CPE for cations which is dependent on each cation nature. Important parameters for each cations were discussed in the following.

In case of Ag(I), Cu(II) and Al(III) cations, slopes of graphen oxide based paste electrodes are the highest ones. It seems that in case of these cations, the lipophilicity of the paste electrodes is important parameter. In fact the extent of extraction of hydrophilic cations in graphene oxide paste electrode is higher than the others due to the presence of oxide groups on its surface. So, the lipophilicity of graphene oxide which is lower than other carbon structures can lead to increasing of the polarity in the conducting paste of electrode. As a result, the sensitivity (slope of calibration curve) for determination of these three cations at graphene oxide paste electrode was increased.

On the other hand, the main important electrode parameter for Cr(III) cation is the electrode's conductivity. Slope of calibration curve for Cr(III) cation is the lowest at graphene oxide paste electrode and is higher than the other kinds of utilized carbon pastes at graphite paste electrode. The following order can be explained by conductivity of resulting carbon paste electrode because electrical conductivity of graphite is higher than graphene and carbon nanotube [26]. And also, graphene oxide is known as a low-conductive material. As a result, slope of calibration curve for graphite paste electrode is higher than the others and graphene oxide paste electrode results lower sensitivity.

For Fe(III) and Hg(II) cations, graphene paste electrode presents super Nernstian behavior rather than other three electrodes. This property is probably due to the three advantages of graphene, i.e. possessing nano sized particles, high conductivity and high surface area. Although the conductivity of graphite is higher than the other carbon allotropes but graphite is a micro-sized carbon powder. So in case of Fe(III) and Hg(II), graphene (as a nanostructure material) with high conductivity shows the higher slope rather than graphite based paste electrode. On the other hand, graphene presents higher surface area for elec-

Table 2. Linear ranges (mol L^{-1}) of different carbon paste electrodes with different carbon nanostructures

	Ag^+	Cu^{2+}	Hg^{2+}	Fe^{3+}	Cr^{3+}	Al^{3+}
Graphite	1.5×10^{-6}–6.7×10^{-3}	1.1×10^{-7}–5.4×10^{-5}	3.3×10^{-5}–5.2×10^{-5}	6.7×10^{-7}–3.1×10^{-4}	8.5×10^{-5}–2.5×10^{-2}	3.7×10^{-4}–3.4×10^{-3}
CNT	1.3×10^{-6}–6.6×10^{-3}	3.0×10^{-5}–3.5×10^{-4}	3.3×10^{-5}–5.23×10^{-5}	4.0×10^{-8}–1.6×10^{-5}	6.4×10^{-5}–3.0×10^{-2}	2.7×10^{-4}–6.6×10^{-3}
Graphene oxide	1.5×10^{-6}–5.7×10^{-3}	9.3×10^{-9}–9.5×10^{-5}	1.3×10^{-6}–5.0×10^{-5}	9.3×10^{-8}–1.1×10^{-4}	1.6×10^{-5}–3.1×10^{-2}	3.5×10^{-4}–5.5×10^{-3}
Graphene	1.0×10^{-6}–6.2×10^{-3}	1.1×10^{-7}–9.2×10^{-5}	8.0×10^{-7}–4.8×10^{-5}	1.2×10^{-7}–2.4×10^{-6}	4.8×10^{-5}–2.5×10^{-2}	2.7×10^{-4}–4.7×10^{-3}

tron transfer rather than multi walled-carbon nanotube. As a result, slope of calibration curve for graphene-based electrode is higher than other three electrodes.

The best responses (Nernstian response) for Ag(I), Cu(II) and Al(III) can be observed at graphite paste electrode, while in case of Fe(III), CNT paste electrode shows more appropriate Nernstian responses. However it is noteworthy that CNT paste electrode showed good Nernstian slope on CNT paste electrode. In case of Hg(II), responses of all paste electrode are almost near to each other and all of them are super Nernstian, however the response of graphene paste electrode is higher than the others. For Cr(III), the near Nernstian response can be observed for graphene oxide paste electrode. Totally, the responses of graphene oxide paste electrode show the worst response rather than the other carbon paste electrodes. Probably, this is due to its non-conductivity and disrupted sp^2 bonding networks [27].

Comparison of Linear Ranges and LODs

Another parameter is linear range of calibration curve. The linear ranges for all experiments are shown in Table 2. For all cations, linear ranges of all nanostructure based carbon paste electrodes (i.e. CNT, graphene and graphene oxide) are wider than graphite based one. So, carbon nanomaterials certainly offer significant advantages in the construction of carbon paste electrodes. The linear ranges for Cu(II), Hg(II) and Fe(III) at graphene and graphene oxide paste electrodes are increased about one or even two order of magnitude rather than conventional carbon paste electrode.

LOD is another parameter which ascribed by crossing point of two straight lines in low analyte concentrations. The best LOD for Ag(I) and Hg(II) cations were observed at graphene paste electrode while for Cu(II) and Cr(III), the best values were seen at graphene oxide paste electrode. Also the best LOD for Fe(III) was obtained by carbon nanotube paste electrode (data not shown but the values of LODs are almost near to the low limit of linear ranges shown in Table 2).

The better results can be evaluated by considering all three parameters, i.e., slopes, linear ranges and LODs of all cations. Clearly, slope, LOD and linear range for Hg(II) at graphene paste electrodes is lower than other carbon paste electrodes and thus this electrode is more acceptable. In case of Fe(III) ion, the best slope, LOD and linear range were observed at CNT paste electrode. Also for Cr(III) cation, more satisfied results (slope, linear range and LOD) were obtained at graphene oxide paste electrode. So, it seems that exchanging the micro-sized graphite with nanostructure carbon materials can cause an improvement in potentiometric response of carbon paste electrode.

Response Time

Another important parameter for a potentiometric sensor is its response time which defined as a required time to reach 90% of final potentiometric response. Because Cu(II) for all electrodes shows near Nernstian response, solution of 0.1 mM of this cation were used to obtain response time. Experiments were repeated seven times and corresponding average times for graphite, graphene, graphene oxide and CNT based carbon paste electrodes were obtained as 9.4 ± 0.9, 6.7 ± 0.6, 4.9 ± 0.4 and 6.3 ± 0.6 s, respectively. Clearly, response time of all carbon nano-materials is lower rather than conventional carbon paste electrode. Also, the response time for graphene oxide paste electrode is faster rather than the other electrodes. The faster response time at this electrode is accompanied with super Nernstian behavior for Cu(II) cation. This behavior is probably due to the low conductivity of graphene oxide and presence of huge number of oxide groups on its surface.

Electrode Stability

The stability of all electrodes were examined in solution of 1 mM Cu(II). Potentiometric responses of all electrodes during 60 min were depicted in Fig. 1. Obviously, potential response of paste electrodes con-

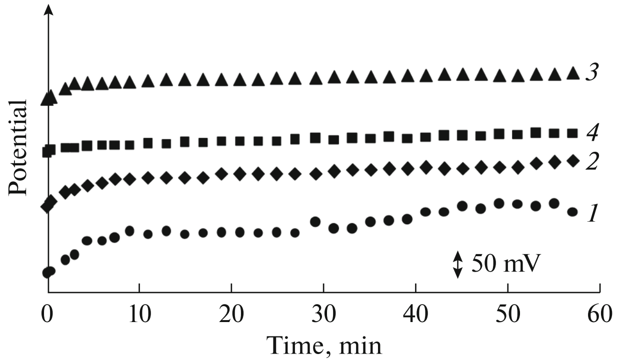

Fig. 1. Stability response of (*1*) graphite, (*2*) carbon nanotube, (*3*) graphene and (*4*) graphene oxide paste electrodes during 60 min in 1 mM Cu(II) solution.

tained graphene and graphene oxide are more stable than two other kinds of electrodes. During 60 min, responses of graphite, carbon nanotube, graphene, graphene oxide paste electrodes were changed about 92, 64, 37 and 27 mV, respectively.

CONCLUSIONS

According to potentiometric results of four kinds of CPEs contained different allotropes of carbon, it was observed that potentiometric behavior is different in analysis of different cations with different charges and properties. It could be concluded that in spite of completely clear benefits of carbon nanostructures in electrochemistry, each allotrope of carbon show a bold advantage in determination of a specification. Micro-sized graphite in carbon paste electrode was replaced with carbon nanostructures including graphene, graphene oxide and multi-walled carbon nanotube. Then potentiometric responses of these carbon paste electrodes were compared to each other. Based on the calibration curves for six different cations, changing the conductive phase of carbon paste electrodes into the nano-sized ones can improve the potentiometric response of corresponding paste electrode. Slope of the calibration curves for four cations including Cu(II), Hg(II), Cr(III) and Fe(III)was improved when carbon nanomaterials were used. Also, by using nanostructures in construction of carbon paste electrode, linear ranges for all cations were wider and LOD in almost all cases were improved. Stability of graphene and graphene oxide paste electrodes in aqueous solution of Cu(II) is better than the others. In case of response time toward Cu(II) solution, the best results were obtained at graphene oxide paste electrode. The obtained information can be utilized for better designing of modified carbon paste electrode as a selective electrode.

ACKNOWLEDGMENT

The authors wish to acknowledge the support of this work by Islamic Azad University Research Council.

REFERENCES

1. Švancara, I., Vytřas, K., Barek, J., and Zima, J., *Crit. Rev. Anal. Chem.,* 2001, vol. 31, p. 311.
2. Švancara, I., Vytřas, K., Kalcher, K., Walcarius, A., and Wang, J., *Electroanalysis,* 2009, vol. 21, p. 7.
3. Lindquist, J., *J. Electroanal. Chem. Interfacial Electrochem.,* 1974, vol. 52, p. 37.
4. Kalcher, K., Kauffmann, J.-M., and Wang, J., *Electroanalysis,* 1995, vol. 7, p. 5.
5. Stanić, Z. and Girousi, S., *Sens. Electroanal.,* 2011, vol. 6, p. 89.
6. Safavi, A., Maleki, N., Honarasa, F., Tajabadi, F., and Sedaghatpour, F., *Electroanalysis,* 2007, vol. 19, p. 582.
7. Švancara, I. and Schachl, K., *Chem. List.,* 1999, vol. 499, p. 490.
8. Lowinsohn, D., Gan, P., Tschulik, K., Foord, J.S., and Compton, R.G., *Electroanalysis,* 2013, vol. 25, p. 2435.
9. Maleki, N., Safavi, A., and Tajabadi, F., *Anal. Chem.,* 2006, vol. 78, p. 3820.
10. Safavi, A., Maleki, N., Aghakhani Mahyari, F., and Doroodmand, M.M., *Fullerenes, Nanotub. Carbon Nanostructures,* 2013, vol. 21, p. 472.
11. Wang, J., *Electroanalysis,* 2005, vol. 17, p. 7.
12. Shao, Y., Wang, J., Wu, H., Liu, J., Aksay, I., and Lin, Y., *Electroanalysis,* 2010, vol. 22, p. 1027.
13. Mordkovich, V.Z. and Karaeva, A.R., *Fullerenes, Nanotub. Carbon Nanostructures,* 2010, vol. 18, p. 516.
14. Goze, C., Vaccarini, L., Henrard, L., Bernier, P., Hemandez, E., and Rubio, A., *Synth. Met.,* 1999, vol. 103, p. 2500.
15. Kaneto, K., Tsuruta, M., Sakai, G., Cho, W. Y., and Ando, Y., *Synth. Met.,* 1999, vol. 103, p. 2543.
16. Valentini, F., Amine, A., Orlanducci, S., Terranova, M.L., and Palleschi, G., *Anal. Chem.,* 2003, vol. 75, p. 5413.
17. Rivas, G., Rubianes, M.D., Pedano, M.L., Ferreyra, N.F., Luque, G.L., Rodríguez, M.C., and Miscoria, S., *Electroanalysis,* 2007, vol. 19, p. 823.
18. Yang, W., Ratinac, K.R., Ringer, S.P., Thordarson, P., Gooding, J.J., and Braet, F., *Angew. Chem. Int. Ed. Engl.,* 2010, vol. 49, p. 2114.
19. Chen, M.L., Park, C.Y., Meng, Z.D., Zhu, L., Choi, J.G., Ghosh, T., Kim, I.J., Yang, S., Bae, M.K., Zhang, F.J., and Oh, W.C., *Fullerenes Nanotub. Carbon Nanostructures,* 2013, vol. 21, p. 525.
20. Alwarappan, S., Erdem, A., Liu, C., and Li, C., *J. Phys. Chem. C,* 2009, vol. 113, p. 8853.
21. Wang, Y., Li, Y., Tang, L., Lu, J., and Li, J., *Electrochem. Commun.,* 2009, vol. 11, p. 889.
22. Kovtyukhova, N.I., Ollivier, P.J., Martin, B.R., Mallouk, T.E., Chizhik, S., Buzaneva, E.V., and Gorchinskiy, A.D., *Chem. Mater.,* 1999, vol. 11, p. 771.
23. Wang, Y., Li, Y., Tang, L., Lu, J., and Li, J., *Electrochem. Commun.,* 2009, vol. 11, p. 889.
24. Shamsipur, M., Tashkhourian, J., Hemmateenejad, B., and Sharghi, H., *Talanta,* 2004, vol. 64, p. 590.
25. Ceresa, A., Sokalski, T., and Pretsch, E., *J. Electroanal. Chem.,* 2001, vol. 501, p. 70.
26. Marinho, B., Ghislandi, M., Tkalya, E., Koning, C.E., and With, G., *Powder Technol.*, 2012, vol. 221, p. 351.
27. Dreyer, D.R., Park, S., Bielawski, C.W., and Ruoff, R.S., *Chem. Soc. Rev.,* 2010, vol. 39, p. 228.