10.17951/aa.2019.74.2.41-52

ANNALES
UNIVERSITATIS MARIAE CURIE-SKŁODOWSKA
LUBLIN – POLONIA

VOL. LXXIV, 2 SECTIO AA 2019

Characteristics of carbon nanomaterials and their application in the construction of potentiometric sensors – review

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Carbon nanomaterials have been very popular in the scientific community in recent years, because of their unusual physical and chemical properties. Their high electrocatalytic activity, very good electrical conductivity and mechanical resistance mean that scientists are constantly looking for new technological solutions to take advantage of the opportunities offered by nanomaterials in many areas of human activity. One of such area are potentiometric sensors. There are many publications in which scientists describe methods of construction, analytical parameters and practical applications of new sensors obtained using carbon nanomaterials, and often also describe methods of synthesis of new original nanomaterials. The purpose of this work was to characterize carbon-based nanomaterials and their application in the construction of ion-selective electrodes.

Keywords: potentiometry, ion-selective electrodes, potentiometric sensors, nanoparticles, carbon nanomaterials.

1. INTRODUCTION

Humanity has been striving to create great things for thousands of years. Larger temples, palaces, skyscrapers, ships, planes ... However, this trend has been decreasing for several dozen years, giving way to the desire to obtain materials of smaller and smaller sizes, the desire to learn about emerging structures and their properties on a microscale, and over time also nanoscale. Today, nanomaterials that surround us, and from the consumers' point of view, rather the products for which they were used, are rather everyday. Nanomaterials have been used in many industries, including various areas, such as sanitary coatings, in some sunscreens, and even toothpastes and food products [1].

Potentiometric sensors are a rapidly growing field of science using nanomaterials in recent years. Among them, the most popular are ion-selective electrodes (ISEs), which have been used by scientists for over a hundred years to measure the pH of solutions and determine the content of many ions in aqueous solutions, both inorganic and organic in the presence of interfering ions. To carry out the researches, a cell consisting of two electrodes (indicator electrode and reference electrode) is needed, whose electromotive force (EMF) is measured. ISEs owe their popularity to, among others easy operation and low equipment costs as well as small dimensions. In addition, they have low detection limits, high selectivity and short response times.

For many years nanomaterials have been enjoying unflagging popularity due to their unique electrical properties and high mechanical resistance. To date, in the construction of ISEs have been used many types of carbon nanomaterials, which are currently the most widely studied synthetic nanomaterials. There are many works describing the manufacture and use of sensors for the construction of which they were used, among others: single- and multi-walled carbon nanotubes (SWCNTs [2–4] i MWCNTs [5–8]), graphene [9, 10], chemically and electrochemically reduced graphene oxide (CRGO [11, 12] and ERGO [13]), fullerenes [14], mesoporous carbon with colloidal print (CIM) [15], amorphous carbon in the form of carbon black [16] or three-dimensional ordered microporous carbon (3DOM) [17]. These and many other carbon nanomaterials have been successfully used as solid contact in ion-selective electrodes, obtaining sensors with very good potential stability, resistant to many external factors and easier to miniaturize compared to their classic predecessors.

2. ION-SELECTIVE ELECTRODES WITH SOLID CONTACT

Ion selective electrodes belong to the group of potentiometric sensors, whose history dates back to the beginning of the 20th century. These are proven tools widely used in many areas of human activity enabling the provision of information on the concentration (more precisely activity) of main ions in the presence of other interfering ions based on the measurement of the electrode potential [18]. They are used in clinical analysis and the pharmaceutical industry, in food production and agriculture as well as in environmental monitoring [19]. The most important element of ISEs is certainly the ion-sensitive membrane, which in classic electrodes with an internal solution (containing the same ions to which the membrane is sensitive) separates it from the sample solution. The composition of such a membrane, depending on the parameters of the electrode and its electrical and mechanical properties, can be optimized. In the most general case, it contains about 65% by weight of plasticizer and about 30% by weight of polyvinyl chloride (PVC), while the rest are additives: ion exchanger and ionophore [18].

In order to obtain better analytical parameters, the classic ISEs were modified by depriving them of an internal solution, the presence of which forced the electrode to be positioned vertically, caused problems in miniaturization and changing the shape of the sensors. In the 1970s, it was proposed to directly apply a plastic PVC membrane to the surface of an electrode, obtaining the coated-wire electrode (CWE). Unfortunately, the combination of two materials with different types of conductivity worsened the repeatability and stability of the electrode potential. Many solutions were tried, but the most promising was to place between them the so-called solid contact characterized by both ionic and electronic conductivity [12, 18].

Ion-selective electrodes with solid contact (SC-ISEs) have a number of advantages over conventional electrodes. The use of solid contact enabled obtaining electrodes with satisfactory analytical parameters, which are also easy to store and can operate in any position and configuration. Due to the lack of an internal solution, they are also simpler to use, easier to transport and to miniaturize [20]. In addition, they help to achieve lower detection limits and are mechanically more resistant due to placing a thicker membrane on a solid base. A comparison of the structure of a classic ISE and a SC-ISE is presented in Figure 1.

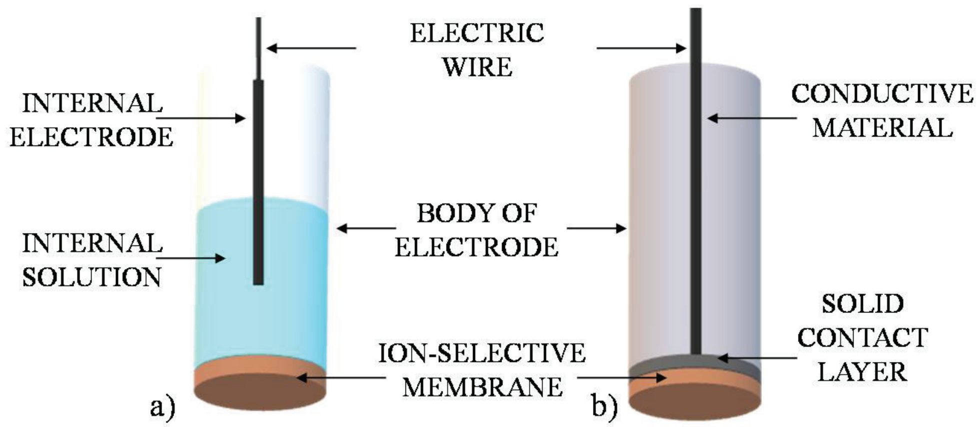

Fig. 1. Electrode construction: a) classic ISE (with internal solution), b) SC-ISE (with solid contact).

The first substance used as an intermediate layer between the membrane and the internal electrode was a conductive polymer, polypyrrole (PPy) [21]. Later, chemical compounds from this group were also commonly used, such as poly (3-octylthiophene) (POT) [22] and poly (3,4-ethylenedioxythiophene) (PEDOT) [23]. Unfortunately, electrodes based on conductive polymers were sensitive to changes in redox potential in solution and the presence of oxygen and carbon dioxide.

3. CHARACTERISTICS OF CARBON NANOMATERIALS AND THEIR APPLICATION FOR CONSTRUCTION OF SC-ISEs

Nanomaterials have unique physical and chemical properties. These are materials with sizes ranging from 1 to 100 nm in at least one dimension [24]. They are characterized by very good electrical conductivity and excellent electrocatalytic activity. They also have a large surface to volume ratio and are very mechanically strong.

In recent years, due to the growing interest in nanoparticles and nanomaterials, scientists are constantly looking for them new applications in various areas. They also began to be used as solid contact in ISEs. In ISEs, they perform the function of an ion-electron converter, the use of which between the ion-selective membrane and the electron conductor enables obtaining solid contact electrodes. Electrodes based on these materials have excellent metrological and electrical parameters, are not sensitive to oxygen, carbon dioxide and light, and have long-term potential stability [4].

There are two types of design possibilities for ion selective electrodes with solid contact. In the first case, solid contact is placed as an intermediate layer between the substrate and the ion-sensitive membrane, while in the second case – carbon nanomaterials are directly introduced into the mixture of components of the ion-sensitive membrane and the whole is homogenized (so-called single piece electrode), and then spotted on the properly prepared electrode surface [6].

Metal nanoparticles (such as gold [25] and platinum [26] nanoparticles) have already been successfully used as intermediate layers. In recent decades, there has also been a lot of scientific work on the use of carbon nanomaterials as a solid contact in ISEs.

Carbon nanotubes were discovered in 1991 and since then they have been constantly enjoying great interest. They are made of graphite sheets (graphene) rolled into a cylindrical form, in which carbon atoms occur in sp^2 hybridization to form a honeycomb structure. Depending on the number of layers, single-wall carbon nanotubes (SWCNTs) and multi-wall carbon nanotubes (MWCNTs) are distinguished [27, 28]. Their structures are shown in Figure 2. Carbon nanotubes are characterized by fast electrode kinetics and better electronic properties than other types of carbon. Sensors based on them therefore show faster electron transfer kinetics and a lower limit of detection than ordinary carbon electrodes. Electrode performance can be influenced by many factors, from nanotube synthesis methods and the type of surface modification, electron mediator additions to the electrode attachment method [28]. The main techniques for the synthesis of carbon nanotubes include: laser ablation, arc discharge and chemical vapor deposition. Carbon nanotubes are used in various areas of human life, in engineering and medicine, for the production of electrical and optoelectronic devices, nanocomposites as well as chemical sensors and biosensors [29]. They also have many environmental applications. They are used in anti-body agents, sorbents, high-flow membranes and environmental sensors as well as in technologies for preventing pollution and obtaining renewable energy [30].

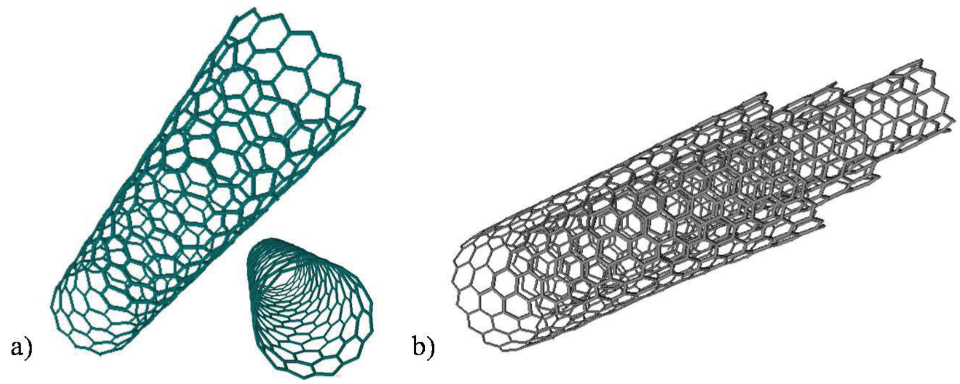

Fig. 2. a) Single-walled carbon nanotube, b) Multi-walled carbon nanotube.

In 2003, Krivenko et al. received SWCNTs by evaporating an electric arc using a nickel-oxygen catalyst. Based on later studies, they showed that the electrochemical properties of such electrodes are similar to those of glassy carbon [2]. In 2011, a paper was published on the production of SC-ISEs using SWCNTs to determine the concentration of surfactants (hexadecyltrimethylammonium ion (CTA^+) and sodium dodecyl ion (SD^-) with a satisfactory lifetime of about three months and acceptable selectivity for other popular ions [3]. The Liang group produced ion selective electrodes sensitive to Cu^{2+} and Pb^{2+} ions with SWCNTs and graphene, respectively, used as solid contacts, obtaining detection limits of 10^{-9} mol/dm^3, very good potential stability and fast electrode response time [4].

Ion-selective electrodes for the determination of perchlorates in water using MWCNTs as solid contact were described for the first time in an article from 2009. Their design consisted of a glassy carbon electrode and an ion selective acrylic membrane, between which a 15 µm thick carboxylated MWCNTs layer was placed. Based on the results obtained, it was found that MWCNTS, like SWCNTs, can be successfully used as an electronic converter in SC-ISEs. Sensors with a wide range of linearity (10^{-6}–10^{-2} mol/dm^3) and a low detection limit of $10^{-7.4}$ mol/dm^3 were obtained [5]. MWCNTs have been successfully used as a solid contact also for the construction of ISEs sensitive to Cd^{2+} ions characterized by very good stability and reversibility of the potential and high selectivity. Their effectiveness was tested in real samples – tap water and river water [6]]. MWCNTs was also used as an additional membrane component in ISEs used to determine Cu^{2+} ions, obtaining a very low detection limit – $7.9 \cdot 10^{-11}$ mol/dm^3 [7]. Recently, Liu et al. have constructed single-piece Pb^{2+}-selective electrodes with nanocomposite membrane based on MWCNTs. Despite the fact that the sensor preparation included only one stage in which the ultrasonicated suspension mixture was spotted onto the surface of the golden electrode, they were characterized by a satisfactory slope of the response curve, a wide range of linearity ($2.0 \cdot 10^{-3}$–$2.0 \cdot 10^{-9}$ mol/dm^3) and a very low detection limit ($4.0 \cdot 10^{-10}$ mol/dm^3). In addition, the absence of a water layer and resistance of the sensor to external factors was demonstrated. They were used to determine Pb^{2+} ions in tap water samples [8].

The article Li et al. from 2012 presents the use as an intermediate layer between the membrane and the electrode material of graphene sheets. Sensors with very good slope of the calibration curve (59.2 mV/decade) for K^+ ions and high potential stability were obtained. The authors emphasized that the electrochemical properties of the graphene layer are similar to those of SWCNTs, and its low cost makes these types of electrodes promising devices in terms of mass production and miniaturization[9]. In the work of Pięk et al. ISEs constructed using graphene (or more precisely: graphene–tetrathiafulvalene nanocomposite) have been described. This solution enabled obtaining nitrate sensors with an excellent slope of the response curve (–59.15 mV/decade) in a very wide range of concentrations (10^{-6}–10^{-1} mol/dm^3 NO_3^-), which also have excellent potential reproducibility and significantly lower resistance and potential drift compared to ordinary GCE [10].

Rather new carbon nanomaterials include chemically and electrochemically reduced graphene oxide (CRGNO and ERGNO, respectively). The first of them was used to construct ISEs sensitive to NO_3^- ions in the work of Tang et al., which were successfully used to determine these ions in water samples (tap water, purified water and mineral water) [11]. In 2011, Ping et al. developed an innovative SC-ISE sensitive to K^+ ions based on CRGNO, a material with high hydrophobicity and resistance to O_2 and CO_2. The sensors obtained were characterized by a low detection limit, fast response time and very good potential stability while not having an undesirable water layer [12]. A year later, the same research group published studies on a screen printed potentiometric sensor using ERGNO, this time sensitive to Ca^{2+} ions. Cyclic voltammetry and impedance spectroscopy were used to examine the charge transfer rate and capacity of the double layer. The sensor was again characterized by a very good slope of the electrode characteristics curve and satisfactory analytical parameters, and was also successfully used to determine Ca^{2+} ions in beverage samples [13].

Fullerenes, like other carbon nanomaterials, have enjoyed great interest since their discovery in 1985. They are polyatomic molecules consisting of an even number of carbon atoms (>16) forming a hollow, closed geometric solid (Figure 3). Thanks to their stability and multiplet redox states and the ability to transfer electrons, they have been used in the construction of sensors, in particular biosensors. In 2008, C_{60} fullerenes were successfully used as solid contact in ISEs, receiving sensors with very good potential stability during prolonged use [14].

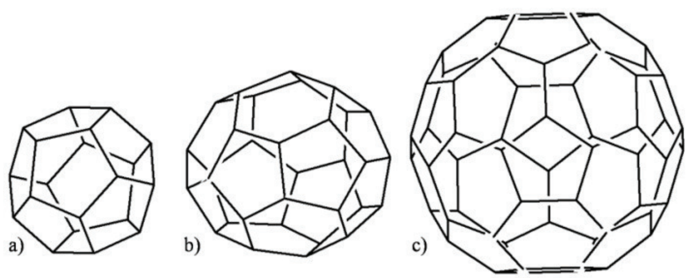

Fig. 3. Fullerene structures: a) C_{20}, b) C_{32}, c) C_{60}.

A new type of SC-ISEs using mesoporous carbon with colloidal print (CIM) is described in a 2014 publication. In addition to preparing sensors, the synthesis of nanomaterials is also comprehensively described in the article. Sensors for the determination of K^+ ions with a Nernst slope of the sensor response curve and a wide range of linearity (59.5 mV/decade in the range: $10^{-5.2}$–$10^{-1.0}$ mol/dm^3), resistant to light, O_2 and CO_2 and extremely stable over time. According to the authors, CIM carbon is easier to prepare and modify, and cheaper compared to other types of carbon materials used as solid contacts, which is why electrodes based on it can be a promising group of SC-ISEs [15].

Amorphous carbon in the form of soot has also been attempted to be used as solid contact in ISEs. This fluffy fine black powder with a large specific surface area, is mainly composed of carbon.

Table 1. Comparison of parameters of solid contact ISEs constructed using carbon-based nanomaterials.

Transducer	Analyte	Slope [mV/decade]	Linearity range [mol/dm^3]	Detection limit [mol/dm^3]	Ref.
SWCNTs	SD^-	59.5	$9.0 \cdot 10^{-5} - 5.0 \cdot 10^{-3}$	$1.9 \cdot 10^{-6}$	[3]
	CTA^+	57.2	$3.0 \cdot 10^{-5} - 7.0 \cdot 10^{-4}$	$5.2 \cdot 10^{-6}$	
	Cu^{2+}	29.8	$1.0 \cdot 10^{-8} - 1.0 \cdot 10^{-4}$	$4.0 \cdot 10^{-9}$	[4]
MWCNTs	ClO_4^-	57.0	$1.0 \cdot 10^{-6} - 1.0 \cdot 10^{-2}$	$4.0 \cdot 10^{-8}$	[5]
	Cd^{2+}	30.2	$1.0 \cdot 10^{-8} - 1.0 \cdot 10^{-2}$	$2.3 \cdot 10^{-9}$	[6]
	Cu^{2+}	8.2	$1.0 \cdot 10^{-10} - 1.0 \cdot 10^{-5}$	$7.9 \cdot 10^{-11}$	[7]
	Pb^{2+}	29.0	$2.0 \cdot 10^{-9} - 2.0 \cdot 10^{-3}$	$4.0 \cdot 10^{-10}$	[8]
graphene	K^+	59.2	$3.2 \cdot 10^{-5} - 1.0 \cdot 10^{-1}$	$1.0 \cdot 10^{-5}$	[9]
	NO_3^-	59.1	$1.0 \cdot 10^{-6} - 1.0 \cdot 10^{-1}$	$6.3 \cdot 10^{-7}$	[10]
CRGO	NO_3^-	57.9	$1.0 \cdot 10^{-5} - 1.0 \cdot 10^{-1}$	$5.0 \cdot 10^{-5}$	[11]
	K^+	58.4	$1.6 \cdot 10^{-6} - 1.0 \cdot 10^{-1}$	$6.3 \cdot 10^{-7}$	[12]
ERGO	Ca^{2+}	29.1	$2.5 \cdot 10^{-6} - 2.5 \cdot 10^{-2}$	$1.6 \cdot 10^{-6}$	[13]
fullerenes	K^+	46.0	–	–	[14]
CIM	K^+	59.5	$6.3 \cdot 10^{-6} - 1.0 \cdot 10^{-1}$	$2.5 \cdot 10^{-6}$	[15]
carbon black	K^+	58.8	–	$7.9 \cdot 10^{-7}$	[16]
		59.1	–	$4.0 \cdot 10^{-7}$	

Depending on the methods of its production and processing, on its surface there are different active groups that affect the final electrochemical behavior of materials. The big advantage of carbon black is the low cost of production and its high conductivity and hydrophobicity. The influence of carbon black addition was observed on the example of ISEs sensitive to K^+ ions. Soot similarly to other carbon nanomaterials, also significantly improved the analytical parameters of the sensors, which showed a very good slope of the response curve and high stability and reproducibility of the potential [16].

Three-dimensional ordered microporous carbon (3DOM) was first used in the construction of SC-ISEs in 2009. They were used to detect trace concentrations of Ag^+ and K^+ ions. Thanks to the two-stage conditioning procedure and optimization of the polymer content and molar ratio of ion and ionophore sites, very low detection limits of $1.6 \cdot 10^{-7}$ mol/dm^3 and $4.0 \cdot 10^{-11}$ mol/dm^3, were obtained [17].

In Table 1 a comparison of selected parameters of ISEs with carbon nanomaterials used as solid contact is presented.

4. CONCLUSIONS

Both ISEs and carbon nanomaterials have many advantages, which is why, as expected, their combination proved to be a very fruitful step in the development of new ISEs. Over the past decades, there has been a lot of scientific publications about the use of carbon nanomaterials as a solid contact in ISEs. Their attractiveness in this aspect is associated primarily with their excellent electrical properties and also significant reduction of the water layer between the electrode substrate and the ion-selective membrane and the resistance of the electrodes constructed with their use to light, carbon dioxide or oxygen. Attempts at miniaturization of sensors and the construction of multi-sensor analytical platforms are also underway, in which nanomaterials can play a large role. Scientists are successfully striving to obtain ever new nanomaterials for their subsequent use in the construction of SC-ISEs with satisfactory parameters for the determination of a wide range of chemical compounds.

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