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Polymer nanocarbon materials as ion-to-electron transducers in solid-contact ion-selective electrodes

Konstantin Yu. Zhizhin[a], Evgeniy S. Turyshev[b], Aleksander V. Kopytin[c], Liliya K. Shpigun[d],
Nikolay T. Kuznetsov, Nikolay P. Simonenko, Natalya N. Zamyatina[e],
Mukhammadislom S. Madraimov, Gleb I. Betenev

N. S. Kurnakov Institute of General and Inorganic Chemistry of Russian Academy of Sciences, Moscow, Russia

[a]kyuzhizhin@igic.ras.ru, [b]tyrishev@gmail.com, [c]ionix@igic.ras.ru,
[d]liliaspigun@gmail.com,[d]shpigun@igic.ras.ru, [e]yatina_76@bk.ru

Corresponding author: Liliya K. Shpigun, liliaspigun@gmail.com, shpigun@igic.ras.ru

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ABSTRACT Carbon nanoparticles materials in polymer modification have gained particular importance in modern potentiometric studies after they were discovered to be ion-to-electron transducers in solid-contact ion-selective electrodes (SC-ISEs). This paper describes the preparation and comparative evaluation of poly(vinyl chloride) (PVC) and Nafion membranes incorporated with light fullerene C60, single carbon nanotubes (SWCNTs) and their mixture as transducer interlayers in the SC-ISE based on the ion-sensing PVC-membrane containing a high lipophilic 2-[bis-octadecyl sulfonic)-*closo*-decaborate anion. The best electroanalytical performance was achieved for the sensor fabricated with the transducer made by combining two transducing layers, a Nafion film modified with fullerene C60 and a plasticized PVC film modified with SWCNTs-C60 hybrid filler, which were sequentially applied onto the substrate carbositall electrode surface. The test results showed that the newly prepared a layer-by-layer SC-ISE is suitable for the sensitive determination of local anesthetics and some other protonable nitrogen-containing drugs.

KEYWORDS nanocarbon-doped polymers, fullerene C60/SWCNTs, solid-contact ion-selective electrode, ion-to-electron transducing materials, local anesthetics.

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1. Introduction

Over the last few years, the development of nanostructured materials as ion-to-electron transducers in solid-contact ion-selective electrodes (SC-ISEs) is of a great interest in the electroanalytical chemistry [1]. SC-ISEs are asymmetric devices, in which an ion-sensing membrane (ISM) contacts with a solid-contact layer (ion-to-electron transducer) on one side, and with the sample solution to be analyzed on the other side (Fig. 1).

Nikolsky and Materova were the first to propose some basic criteria for manufacturing SC-ISEs with stable and reproducible potentials measured under open circuit conditions [2]. Currently, it is a reversible mechanism of transition from ion current to electron current, high bulk capacity to produce a stable potential, high degree of hydrophobicity to eliminate the undesirable water layer between the electron conductor and the ISM, and the absence of side reactions in the ion-to-electron transduction process. Although the range of available materials with ionic-electronic hybrid conductivity is extensive, carbon nanoparticles (CNPs) are particularly favored. The high hydrophobicity, chemical stability, large electric double-layer (EDL) and remarkable charge-transfer capability provide CNPs some advantages over other ion-to-electron transducers [3]. However, self-aggregation or rearrangement due to strong van der Waals interactions between neighboring sheets can lead to loss of their active surface area and electrical conductivity. The incorporation of CNPs in polymer matrices assists in overcoming these difficulties [4–7].

It should be noted that traditional carbon-based electrodes like graphite, glassy carbon or carbositall directly coated with an ISM can also be considered as solid-contact potentiometric sensors. The electrochemical process can occur by a purely electronic mechanism due to the transfer of free electrons from the polyconjugate system of graphite-like carbon crystallites to the adsorbed or dissolved potential-determining ions. Unfortunately, in this case, the resulting EDL has a very small capacitance, which leads to a poor reproducibility and a significant drift of the standard electrode potential (E'_o) during the time [8]. To solve the historical problem of poor potential stability, it has been proposed to disperse carbon

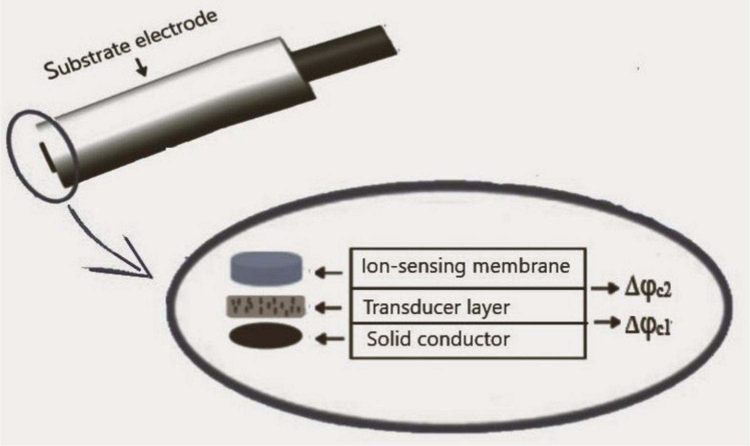

FIG. 1. Schematic representation of SC-ISEs based on the solid contact with CNPs

nanoparticles (CNPs) directly into the polymer membrane composition [9–11] or to include an ion-to-electron transducer layer (SC-layer) as an intermediate support between the polymer ISM and the solid conductor [12–15].

Different types of polymers and nanofillers have been proposed so far to prepare SC-transducers. Remarkable examples of using nanocomposites of conducting polymers (CPs) with CNPs have been reported [16–24]. However, most of CPs can have drawbacks such as high electroactivity that promotes non-specific chemical reactions, sensitivity to CO_2, pH or light. In addition, the formation of an undesirable aqueous film between the ISM and the inner SC is often observed [25, 26]. From our point of view, it is of interest to prepare solid-contacts by using CNPs-doped non-conductive polymer matrices, as they seem to form three-dimensional nanostructures that can provide a significant improvement in the performance characteristics of SC-ISEs. The incorporation of CNPs into polymer matrices is explored as a strategy to obtain composite materials with electrical properties. In particular, the creation of conductive nanocomposites of PVC with CNPs (graphene, fullerenes, carbon nanotubes, etc.) and characterization of their specific properties are described in several publications [27–34]. According to the literature, the introduction of CNPs can lower the resistivity of PVC-matrix by several orders of magnitude [28]. For Nafion-CNPs composites, this is mainly achieved through either ionic movement or electron self-exchange between dopant species [35–40]. Recently, the synthesized PVC/mixed graphene-carbon nanotube nanocomposite was proposed for the development of an amperometric Ag^+-sensor [41]. The development of SC-ISE with two PVC-based sandwiched membranes was described [42]. The first membrane contains suspension of halogen salts of silver and alkaline metals as well as silver nanoparticles and is placed on Ag substrate or conducting substrate covered with silver. It acts as a solid contact of an ion-selective electrode when covered with the second PVC membrane sensitive to potassium, sodium or chloride ions. However, as far as we know, there is still no information on using CNPs-PVC composite materials as SC-layers in ISEs.

In this paper, we investigated the possibility to fabricate SC-ISEs, in which the SC-layer was prepared by incorporating single-walled nanotubes (SWCNTs), light fullerene C60 or their hybrid mixture into plasticized PVC- and Nafion-membranes. The primary goal of the study was to evaluate the prepared nanostructured materials as intermediate ion-to-electron transducing layers in the potentiometric membrane sensor based on ion-pair complexes of cesium cation with 2-[bis-octadecyl-sulfonic]-*closo*-decaborate anion ($Cs[B_{10}H_9S(n\text{-}C_{18}H_{37})_2]$). Recently, we have shown that the indicated lipophilic anion demonstrated high sensitivity to cationic protonated forms of local anesthetic drugs [43]. For this reasons, an amino-ester anesthetic procaine (2-diethyl-aminoethyl-4-aminobenzoate) was chosen as a model determinant.

2. Materials and methods

2.1. Reagents and solutions

The commercial carbon nanomaterials, such as fullerene C60 (99.5 %, Bucky USA) and SWCNTs (> 90 %, 0.7–0.9 nm diameter, Aldrich) were used. High molecular weight poly(vinyl chloride) (PVC), Nafion solution (5 % w/w in EtOH), bis(1-butylpentyl)adipate (BBPA) and tetrahydrofuran (THF), procaine hydrochloride (Pro·HCl, 99 %, p/p purity), lidocaine hydrochloride monohydrate (Lid·HCl, 99.9 % p/p purity), articaine hydrochloride (Art·HCl, ≥ 98 % p/p purity), adenine (6-aminopurine, ≥ 99 % p/p purity), adrenaline ((±)-epinephrine hydrochloride, 95 % p/p purity) were purchased from Merck KGaA and used without prior purification. The stock standard solutions of these analytes (0.01 M) were prepared by dissolving precise amounts of each compound in water or 0.001 M HCl. The working standard solutions were prepared daily from the stock solutions by serial dilution. All other chemicals were of analytical or pharmaceutical grade and their solutions were prepared with redistilled water.

2.2. Processing of polymer nanocomposite suspensions

As polymer matrixes for C60 and SWCNTs, we chose PVC and Nafion, which are known to allow a relative uniform distribution of CNPs in the composite volume with their minimal aggregation. Initial suspensions of polymer composites were achieved by dispersing fullerene C60, SWCNTs or their mixture into a plasticized PVC solution, and fullerene C60 into a Nafion alcohol solution under ultrasonic irradiation conditions. In order to reach the better homogeneous distribution of CNPs (SWCNTs and C60) in a plasticized PVC-matrix, a multi-step procedure was used. In the first step, a PVC solution in dry freshly distilled THF (25 w/v %) was prepared by stirring for 3 h at 30 °C. Then, a plasticizer (BBPA) was added to the PVC solution under effective stirring and at room temperature. Finally, an appropriate amount of CNPs was incorporated into the plasticized polymer solution with the aid of irradiation in an ultrasonic water bath during 30 min. The stable C60-Nafion dispersion (0.5 wt. %) was prepared by dissolving the fullerene powder in 2.3 mL of Nafion (2.5 w/v %) followed by ultrasonic treatment of the resulting mixture for about 60 min.

2.3. Preparation of an ion-sensitive membrane precursor solution

Precursor solution of ISM of the following composition (wt. %) was prepared: membrane-active compound – 1.2; plasticizer (BBPA) – 69.8; PVC – 29.0. The components were dissolved in 2.0 mL of dry freshly distilled THF. After the membrane cocktail was homogeneously mixed, it was stored at 4 °C. The electroactive compound ($Cs[B_{10}H_9S(n\text{-}C_{18}H_{37})_2]$) was synthesized and identified in the laboratory of chemistry of light elements and clusters of the N. S. Kurnakov Institute of General and Inorganic Chemistry of RAS [44].

2.4. Potentiometric sensor fabrication

All testing SC-ISEs were fabricated using a carbositall (CS) electrode (Wolta, Russia). Before modification, the CS surface was mechanically polished with 0.3 and 0.05 μm alumina powders. Then, it was thoroughly cleaned by ultrasonication with ethanol and deionized water, in order to remove residual alumina particles. After that, 20 μL of the corresponding PVC-based nanocomposite suspension (in 10 μL aliquots) was applied to the freshly cleaned CS surface and left to dry at 34 °C in a pressure chamber. In case of preparing the bilayer transducer, 10 μL of the C60-Nafion suspension (in aliquots of 5 μL) was firstly deposited onto the CS surface and left to dry for at least 1 h by rotor evaporating at 36 °C under vacuum, forming a thin film with a thickness of approximately 100 μm. Further, the modified electrode was coated with a precursor solution of ISM (in two portions of 25 μL) to form a potentiometric sensor. The ISM thickness was about 400 μm. Before using, each sensor was soaked in 1.0×10–3 M Pro·HCl solution for 24 h, in order to establish the membrane – solution equilibrium. The uptake of water was necessary for reaching stable electrode potentials. The sensors were kept dry in an opaque closed vessel while not in use.

2.5. Measurements

To characterize the prepared SC-ISEs, morphological observation and potentiometric investigation at the room temperature (25 ± 2 °C) were performed. All potentiometric measurements were made with a pH/ion analyzer Radelkis OP-300 "Hungary" by using the following galvanic circuit:

CSE | SC-layer | ISM || Test solution || $KCl_{(satd)}$, AgCl/Ag

The ultrasonic bath (Elmasonic One, Germany, 35-kHz ultrasound) was used in all experiments. The surface morphology of carbon nanomaterials was examined with a scanning electron microscope (SEM, Carl Zeiss NVision 40, Germany).

3. Results and discussion

3.1. Morphological characterization of the polymeric nanocomposite materials

Polymeric matrices filled with CNPs are nanosystems with very strong mechanical and electrical properties, which are mainly due to the interaction between the matrix and the nanofiller. It should be noted, however, that many aspects of nanoparticle diffusion in a polymer are still far from being solved [45]. This is especially related to their possible aggregation both while preparing polymer nanocomposite suspensions and during the formation of the polymer film on the surface of the substrate electrode. Self-aggregation or rearrangement of carbon nanofillers due to strong van der Waals interactions can lead to changes of the effective surface area and the electrical conductivity of composites. Obviously, the homogeneous dispersion of CNPs in the polymer matrix plays a key role in preserving their functionality as ion-electronic transducers.. The literature review in this field showed that one of the ways to achieve a high degree of homogeneity of the polymeric nanocomposite material is the use of ultrasonic processing [46].

Since the potentiometric response of SC-ISEs is related to the physical properties of SC-layers, the morphology of the surface of CNPs-PVC composites was investigated before and after ultrasonication. Observation of the prepared composite materials showed that the dopant distribution in the plasticized PVC-matrix was heterogeneous (Fig. 2).

The aggregated CNPs may be visible, especially in the areas of interstructural defect zones in PVC. The distributed nanofillers are supposed to be aggregated and tend to re-stack to each other, while PVC macromolecules surround them to core shell structure. The ultrasonic treatment leaded to splitting of the bundles and forming micelles, which can be

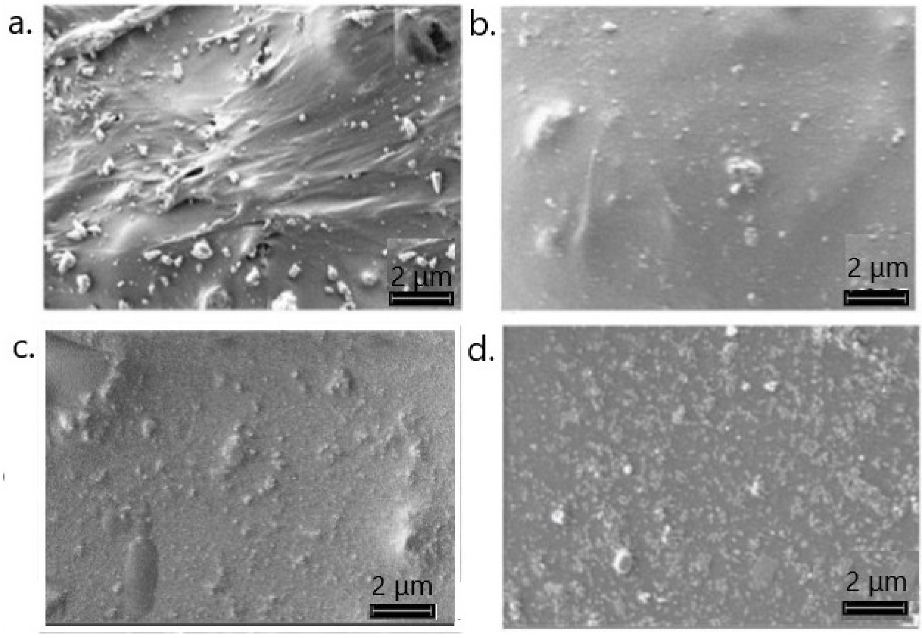

FIG. 2. SEM images of the surface fragments of the plasticized PVC membrane with SWCNT (a, b) and fullerene C60 (c,d) before (a,c) and after (b,d) ultrasonication. The content of nanofillers – 5.0 wt. %

single nanostructures or small-diameter bundles surrounded by plasticizer molecules. The plasticizer probably serves as a carrier of nanoparticles for their distribution in the PVC-matrix [27–30]. It can be assumed the formation of an electrically conductive structure with a segregated scheme of the CNPs arrangement occurs at the polymeric "cores", completely or partially covered by conducting nanofillers. SEM observations demonstrated that the addition of the C60 to SWCNTs improved their dispersibility in the polymeric matrix (Fig. 3).

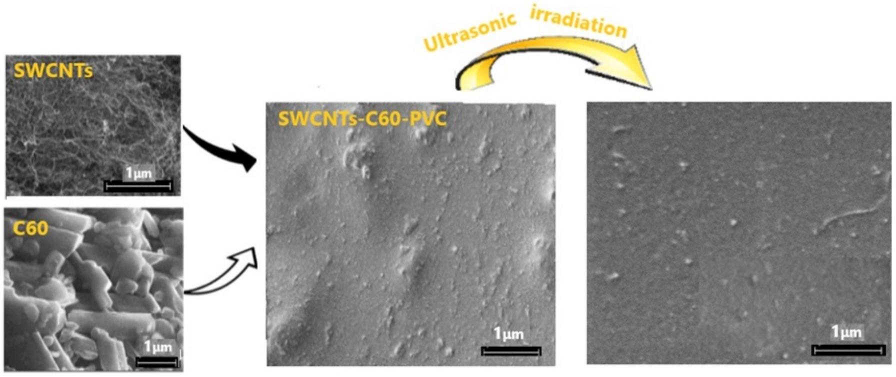

FIG. 3. SEM images demonstrating the formation of the SWCNT-C60-PVC hybrid membrane

Fig. 4 demonstrates the photos of the preparation of C60-Nafion composite membrane. As it can be seen, ultrasonic irradiated C60-Nafion solution has a brown color.

Evidently, the microstructure of Nafion, including the side-pendant (–CF_2–CF_2–) chains and the highly polar sulfonic terminals as well as the crystalline of PTFE, was changed by the dispersion of C60. As indicated earlier, the fullerene can form both non-covalent binding and donor-acceptor complexes with polymers [47]. Being highly hydrophobic and electronically neutral with zero charge on each atom, C60 can be surrounded by the Nafion chain (oligomer). Probably, the fullerene molecules and their agglomerates are mainly located in the hydrophobic phase of the Nafion matrix creating structure defects or additional paths of proton conduction [48, 49].

3.2. Potentiometric performance of the prepared SC-ISEs. Electrode response evaluation

The exact mechanism of functioning of carbon nanomaterials in SC-ISEs has yet to be studied in detail, their behavior as ion-to-electron transducers may be due to electrostatic coupling: the presence of charged ions in an ion-sensitive membrane in close contact with a SC-layer may provide electronic capacitive coupling [50]. The potentiometric response

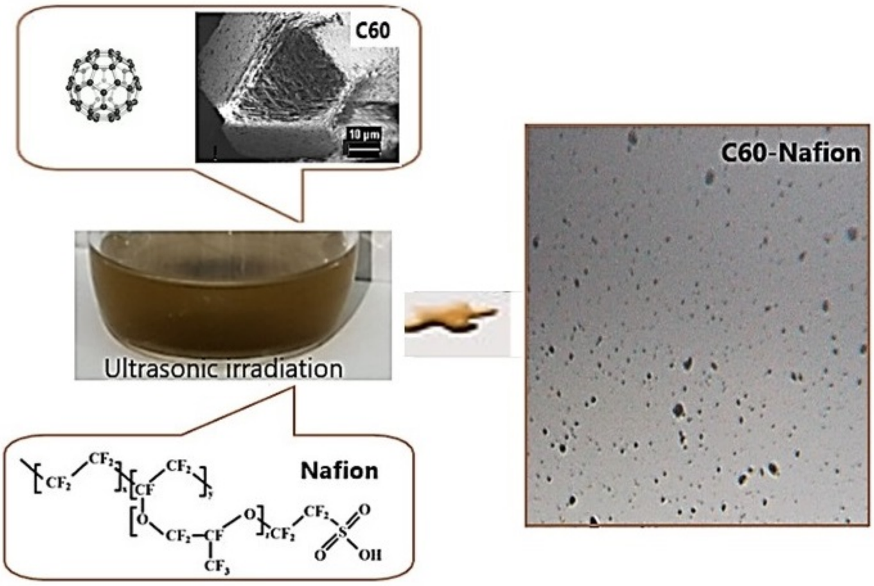

FIG. 4. Schematic illustration of fabrication and photographs of the C60-Nafion composite membrane

of a SC-ISE (E) can be determined by the sum of the interphase potentials, as follows:

$$E = \Delta\varphi_{c1} + \Delta\varphi_{c2} + \Delta\varphi_{c3} \tag{1}$$

The potential jump $\Delta\varphi_{c1}$ at the solid conductor/SC-layer interface is usually very small ($\approx$ 0) since most of the nanomaterials used have a high electronic conductivity. The potential jump $\Delta\varphi_{c2}$ at the SC-layer/ISM interface depends on the amount of charge and the EDL capacitance. If the EDL capacitance is high, the potential change would be small or even near zero. The interfacial potential $\Delta\varphi_{c3}$ at the ISM/solution sample interface can be described by the well-known Nernst equation or by the semi-empirical Nikolsky-Eisenman equation, according to the phase-boundary potential model, which is based on the assumptions of full thermodynamic equilibrium [51, 52]. As a rule, the e.m.f. for the electrochemical cell (E_{cell}) is the sum of all phase boundary potentials and it can be described by the following equation of electrode potential dependence on the logarithm of the ionic activity (a_i):

$$E_{cell} = E'_o + s \log a_i, \tag{2}$$

where s is the slope of a linear electrode response curve; E'_o is a constant for a given galvanic cell, which depends on the reference electrode potential and all interphase potentials, including $\Delta\varphi_{c1}$ and $\Delta\varphi_{c2}$, except of the interphase potential $\Delta\varphi_{c3}$ at the ISM/sample solution interface.

Key parameters for evaluating the potentiometric response of SC-ISEs include its sensitivity to a potential-determining ion, signal stability, and reproducibility of the apparent standard potential (E'_o). These parameters are largely determined by the nature and concentration of nanofillers in the SC-layer. We performed a series of experiments to compare the potentiometric behavior of the sensors fabricated using different CNPs-filled PVC-matrices as SC-layers (Sensors no. 1–6). The corresponding potentiometric response characteristics for the sensors no. 1–3 towards protonated procaine cations are summarized in Table 1. The mean values of standard potentials and slopes were determined on the basis of calibration plots in the concentration range 1×10^{-6} – 0.01 M. As it can be concluded from the obtained results, all prepared sensors provided similar linear calibration graph slopes close to Nernstian response for single-charged ions (slope = 59.2 mV·dec.$^{-1}$, 25 °C) within the wide range of the ProH^{+} activity (concentration). It is obvious that their response towards ProH^{+} is determined by the potential-signal appeared mainly by the ISM/sample solution surface reactions [53]. In contrast, the E'_o value was found to be dependent on the SC-layer composition. This effect is caused primarily by a change in the interphase potential jump $\Delta\varphi_{c2}$ at the SC-layer/ISM interface. In other words, E'_o is largely determined by the nature of CNPs in the SC-layer, their interactions with the polymer matrix and with each other. It is noteworthy that the E'_o obtained for the sensor containing the SC-layer with fullerene nanomolecules is significantly lower than in the case of SWCNTs. This may be due to the special properties of this transducer, in particular to the ability of magical fullerene nanoclusters to non-covalently binding with the plasticized polymer [54].

Remarkably that the E'_o value highly decreased for sensor no. 3 containing the mixture of SWCNTs and C60 (5.0 wt.%, 1:1). More importantly, this effect was accompanied with the reducing the lower limit of detection (LOD) of ProH^{+} cations. Perhaps, the physicochemical characteristics of this material are not simply a sum of fullerenes and nanotubes. The combination of two nanofillers in a polymer matrix can cause a synergistic effect attributed to their

TABLE 1. Comparative data of potentiometric response characteristics of the fabricated SC-ISEs in Pro·HCl solutions (n=5)

Sensor no.	CNPs (5 wt. %)	Slope, mV·dec.$^{-1}$	Linear range, M	LOD, M	Response time, τ_{95} ($\geq 1 \times 10^{-6}$ M)	E'_o, mB
Sensor 1	SWCNTs	59.2 ± 0.3	$9\times10^{-7} - 1\times10^{-2}$	$10^{-6.52}$	10	421.7
Sensor 2	C60	59.0 ± 0.3	$1\times10^{-6} - 1\times10^{-2}$	$10^{-6.40}$	12	124.8
Sensor 3	SWCNTs-C60	58.9 ± 0.2	$5\times10^{-7} - 1\times10^{-2}$	$10^{-7.05}$	7	40.8

large specific surface area and increased electrical properties. This hypothesis can be confirmed by previously published studies [41, 55].

Notably, the potentiometric characteristics of such a sensor depend on the content of SWCNTs and C60 in the SC-layer (Fig. 5). It was found that the increasing the nanofiller concentrations > 5.0 wt.% caused the worsening the electrode response characteristics. Perhaps, the heterogeneity of the polymeric film structure increases in the area of high nanofiller concentrations. It can be associated with the formation of inhomogeneities (fullerene clusters, etc.), which reduce the conductivity of the SC-layer by strengthening the physical network of intermolecular contacts and reducing the free path of charge carriers.

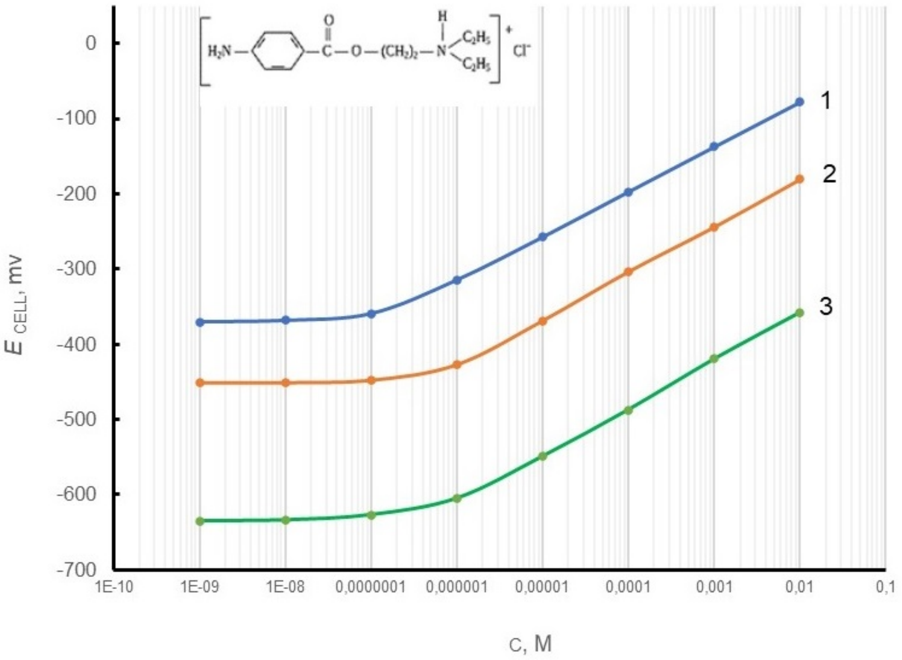

FIG. 5. Electrode functions characterizing the potentiometric response of CS/SWCNT-C60-PVC–ISEs (Sensors no. 3 – 5) towards a protonated procaine cation. The content of the hybrid mixture in SC-layer (wt. %): 1 – SWCNTs/C60 = 2.5/2.5 (Sensor no. 3); 2 – SWCNTs/C60 = 15:5 (Sensor no. 4); 3 – SWCNTs/C60 = 10:10 (Sensor no. 5)

According to the literature, the solid-contact configuration of ISEs appears to be the only approach for wearable potentiometric ion sensing [56, 57]. In view of this goal, the stability of the SC-ISE signal is of crucial importance. A PVC-matrix may exhibit poor mechanical adhesion on electrode substrates. Compared to PVC, Nafion has good adhesion to most electrode surfaces and can protect the surfaces from fouling and deterioration. Therefore, in order to improved potential stability and extend the lifetime of the CS/SWCNT-C60-PVC transducer-based ISE (Sensor no. 3), we have incorporated an additional intermediate layer of C60-Nafion into its construction. Namely, the C60-dopped Nafion-matrix was deposited onto the CSE surface followed by its modification with the SWCNTs- C60-PVC film.

To compare the stability and the reversibility of the potentiometric response of SC-ISEs based on the SWCNT-C60-PVC transducer (Sensor no. 3) and the C60-Nafion/SWCNT-C60-PVC transducer (Sensor no. 6), the both electrodes were inserted one-by-one in 1×10^{-5} M Pro·HCl, 1×10^{-4} M Pro·HCl and finally in 1×10^{-3} M Pro·HCl solution for 30 min, and then changed back to 1×10^{-5} M Pro·HCl solution. The potential was monitored over all these intervals.

It was found that CS/C60-Nafion/SWCNT-C60-PVC-based ISE revealed higher potential stability and reversibility than CS/SWCNT-C60-PVC-based ISE, especially when going back to the more dilute solutions (Fig. 6).

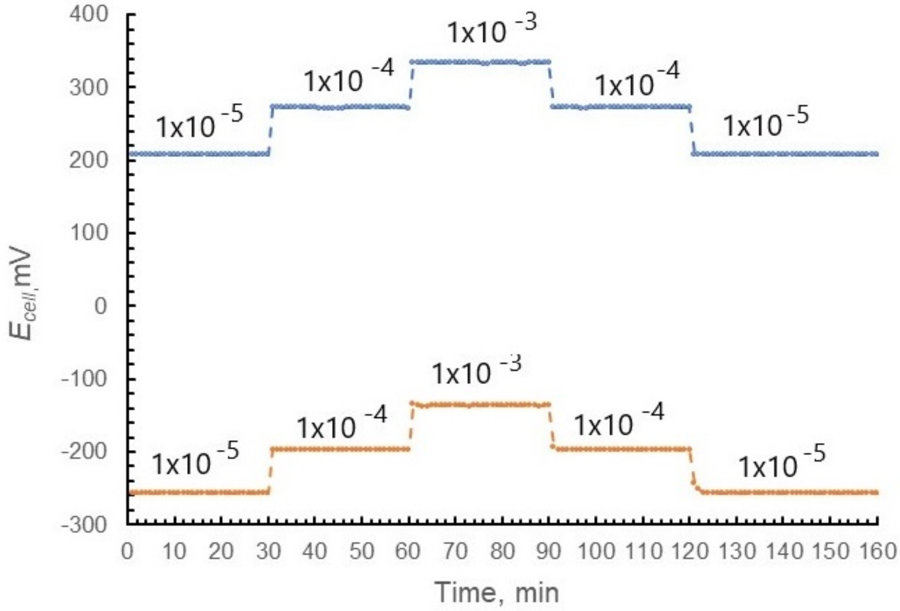

FIG. 6. Reversibility and stability test for (a) CS/SWCNT-C60-PVC–ISE (Sensor no. 3) and (b) CS/C60-Nafion/SWCNT-C60-PVC–ISE (Sensor no. 6) in Pro·HCl solutions (M)

TABLE 2. The analytical performance characteristics of CS/C60-Nafion/SWCNT-C60-PVC/ISM–ISE (Sensor 6) in the solutions of selected protonable nitrogen containing drugs

Sample	E'_o, mB	Slope, mV·decade^{-1}	Linear range, M	LOD, M
Procaine hydrochloride	506.0	58.0 ± 0.1	$1\times10^{-7} - 1\times10^{-2}$	$10^{-7.15}$
Lidocaine hydrochloride	506.7	57.9 ± 0.2	$1\times10^{-7} - 1\times10^{-2}$	$10^{-7.15}$
Articaine hydrochloride	511.9	58.3 ± 0.1	$1\times10^{-7} - 1\times10^{-2}$	$10^{-7.26}$
Adenine (pH 3)	382.1	40.5 ± 0.2	$1\times10^{-7} - 1\times10^{-3}$	$10^{-6.30}$
Adrenaline (pH 3)	295.7	44.9 ± 0.2	$1\times10^{-4} - 1\times10^{-2}$	$10^{-4.40}$

The stability of the potentiometric response was characterized by the level of potential drift that is unrelated to changes in the ionic composition of the sample. It was found that the potential drifts of such electrodes during conditioning in 1×10^{-5} M Pro·HCl were ±0.14 mV h^{-1} and ±0.33 mV h^{-1} for sensor no. 6 and sensor no. 3, respectively. In addition, in case of the sensor no. 6, lower LOD ($10^{-7.15}$) and shorter response time (≤5 s) were achieved, and the standard derivation of a slope of the potentiometric response curve (s) was only 0.12 mV·decade^{-1} (over 7 days). All of these results showed that the addition of the C60-Nafion layer improved the properties of the fabricated SC-ISE and reflected the high efficiency of the layer-by-layer ion-to-electron transducer. In this case, the plasticized SWCNTs-C60-PVC membrane plays the role of a binder (a kind of a porous solid contact) between the ion-sensitive membrane and the C60-Nafion layer.

3.3. Electroanalytical capability

Ion-selective electrodes are selective but not specific. They can respond to a variety of ions in solutions. In case of ion-pair complexes based ISMs, the selectivity is usually controlled by the free hydration energies of the ions and the specificity of their interaction with the binding center. For comparison, we have investigated response characteristics of the newly prepared CS/C60-Nafion/SWCNT-C60-PVC/ISM–ISE towards several important protonable nitrogen containing drugs like procaine. Of course, the ISM pretreatment required the formation of ion-pair complexes of analyte ions with the recognizing compound at the interface between the membrane and solution. Therefore, prior to measurements, the sensor was conditioned in a 1.0 mM solution of each determinant for 1–3 h. When measuring, we took into account that the membrane-active species are the protonated cationic forms of an analyte. As shown in Table 2, the fabricated sensor no. 6

showed a linear response for all analytes tested over a concentration range of almost 4 decades with considerable stability. The sub-Nernstian slopes obtained for adenine and adrenaline is likely due to the partial existence of biprotonated or non-protonated analyte forms in the solutions under study. Overall, the developed sensor can be recommended to the simple and fast control of the protonable nitrogen containing active ingredients in drugs.

4. Conclusion

According to the latest trends, such as the concept of "green chemistry" and "wearable sensors", solid-contact ion-selective electrodes should become excellent inexpensive, low energy and portable devices for the chemical analysis. This work demonstrated that nanocarbon-modified PVC composite materials show high efficiency as ion-to-electron transducers in SC-ISEs with operationally stable and reproducible potentials. The integration of the superior properties of nanocomposite PVC and Nafion membranes made it possible to create a layer-by-layer potentiometric membrane sensor for the highly sensitive determination of procaine and other protonable nitrogen-containing drugs in a wide range of concentrations.

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Information about the authors:

Konstantin Yu. Zhizhin – N. S. Kurnakov Institute of General and Inorganic Chemistry of Russian Academy of Sciences, Leninskii pr.31, Moscow 119991, Russia; ORCID 0000-0002-4475-124X; kyuzhizhin@igic.ras.ru

Evgeniy S. Turyshev – N. S. Kurnakov Institute of General and Inorganic Chemistry of Russian Academy of Sciences, Leninskii pr.31, Moscow 119991, Russia; ORCID 0000-0002-0594-5500; tyrishev@gmail.com

Aleksander V. Kopytin – N. S. Kurnakov Institute of General and Inorganic Chemistry of Russian Academy of Sciences, Leninskii pr.31, Moscow 119991, Russia; ORCID 0000-0003-3366-5167; ionix@igic.ras.ru

Liliya K. Shpigun – N. S. Kurnakov Institute of General and Inorganic Chemistry of Russian Academy of Sciences, Leninskii pr.31, Moscow 119991, Russia; ORCID 0000-0001-9749-2942; liliaspigun@gmail.com; shpigun@igic.ras.ru

Nikolay T. Kuznetsov – N. S. Kurnakov Institute of General and Inorganic Chemistry of Russian Academy of Sciences, Leninskii pr.31, Moscow 119991, Russia; ORCID 0000-0002-2562-6427

Nikolay P. Simonenko – N. S. Kurnakov Institute of General and Inorganic Chemistry of Russian Academy of Sciences, Leninskii pr.31, Moscow 119991, Russia; ORCID 0000-0002-4209-6034

Natalya N. Zamyatina – N. S. Kurnakov Institute of General and Inorganic Chemistry of Russian Academy of Sciences, Leninskii pr.31, Moscow 119991, Russia; yatina_76@bk.ru

Mukhammadislom S. Madraimov – N. S. Kurnakov Institute of General and Inorganic Chemistry of Russian Academy of Sciences, Leninskii pr.31, Moscow 119991, Russia

Gleb I. Betenev – N. S. Kurnakov Institute of General and Inorganic Chemistry of Russian Academy of Sciences, Leninskii pr.31, Moscow 119991, Russia

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