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Development and Characterization of a Recycled Plastic Based Ion-Selective Electrode (PB-ISE) Using CNT Ink as Ion-To-Electron Transducer

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***Abstract*— Environment care is currently a crucial priority due to the increase in worldwide pollution. Nanotechnology and recycled material could be used as a platform to know more easily some analytical ion concentrations. In this investigation, a recycled plastic-based ion-selective electrode (PB-ISE) to use as a potentiometric sensor was built using a transductor material as carbon nanotubes ink (CNT-ink) and a metalized polyester sheet (MPS) from packing residues. To make the electrode, CNT-ink is applied and spread onto the MPS surface adding cycles of 1 ml at 100 °C until a maximal reduction in the electrical resistance and a stable roughness were observed. Once the conductive plastic is ready, it's covered with adherable plastic masks on both sides of MPS to protect it from liquids. The final step is the addition of the ion-selective membrane (ISM) for potassium determination on a circular orifice, which is located on the front mask. The results obtained were compared with a classical solid-contact ion-selective electrode (SC-ISE). Some analytical parameters as sensitivity, linear ranges, and limits of detection of the recycled plastic electrode were comparable with those obtained for the SC-ISE. The best performance was reported for the PB-ISE that afforded a near-Nernstian response (52.08 ± 2.36 mV) with a linear range from 10^{-4} to 10^{-1} M and a limit of detection of 0.0176 mM. The potentiometry technique presents advantages in comparison with other techniques as well as a reduction in the cost and instrumental equipment to measure a wide range of analytes. Also, the straightforward fabrication and robustness that embrace the ISE could create an advantage technique using residual material from food packaging.**

Keywords*— *PB-ISE, CNT, ion-selective membrane.

I. INTRODUCTION

Environment care is currently a crucial priority due to the increase in worldwide pollution [1]. A problem with non-biodegradable plastic material waste increases a global concern due to the high amount of plastic used in food packing [2], [3]. Plastic packaged has a different presentation in food packing and one of them is flexible packages such as coatings, snack packaging, and adhesives. Indeed, the most common flexible packages are polyolefins, polyvinyl and polyesters [4]. Metalized polyester sheet (MPS) is useful with other plastics (PET or PVC) and metals (Aluminum) as snack packing and offers unique advantages and disadvantages [3]. Some advantages could be making it heat sealable and to improve light, gas, and moisture barrier properties [5]. But several disadvantages are presented when the plastic waste material is intended to be recycled. Separation and classification have a main key in the plastic recyclers. Also, microbial contamination and structural integrity of the recycled plastic could be important characteristics that increase the cost and the time of recycling [3], [5]. Since the MPS is used only as food packing, in this investigation a possible reused for this material in planned when a carbon nanotubes ink (CNTs-ink) is applied as a low-priced material for conducting electricity without relevant implications to the environment.

Some authors reported advantages in ISEs when different platforms and nanostructure materials such as CNT are used [6]–[9]. Single-walled carbon nanotubes (SWCNT) and multiwalled carbon nanotubes (MWCNT) display semiconducting and metallic character, working as efficient transducers [10], [11]. CNTs also demonstrate other characteristics such as avoiding the formation of water layers between an ion-selective membrane (ISM) and a solid-contact ion-selective electrode (SC-ISE) [12]. Besides, ISM presents an easy drop cast [13] and avoiding light sensitivity in comparison with conducting polymers where redox reactions occur [7], [14]. Moreover, these particular characteristics make CNTs easy to handle material in practice [6], [11].

Potentiometry is one of the electroanalytical techniques that provide several advantages in comparison with other techniques (IR spectroscopy, UV-spectroscopy, HPLC, Amperometry) [15]–[18]. These techniques are sensitive and selective, but their main drawbacks are the high instrumental cost, technical expertise, long-term analysis and limitation to lab analysis [17], [18]. To overcome some of these problems, potentiometric techniques with ion-selective electrodes (ISEs) could be used. With a suitable ISE, the cost and instrumental equipment would be reduced [14]. Indeed, SC-ISEs and recent paper/plastic-based ion-selective electrodes (PB-ISEs) offer an attractive alternative to conventional analysis. Besides, the ISEs can be easily miniaturized, but a major issue is showed when selectivity is evaluated. As a result, ISM-based sensors

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shown a selectivity pattern that follows the partition coefficients between the aqueous and the organic phases [19]. A selective ionophore is then mandatory to intent to alter this trend. The introduction of this synthetic receptor represents also the main difference with the conventional methods based on enzymatic reactions. The latter methods could suffer from stability or shelf-life issues when employed in a decentralized manner [20], [21].

ISMs are based on plasticized polymeric membrane containing: a polymer (conventionally PVC), a plasticizer, an ion exchanger (to ensure the perm-selectivity of the membrane) and an ionophore (to induce a selectivity pattern). The ionophore (Valinomycin) and the target (Potassium) works on a basic host-guest chemical principle [22]. In this way, several reports have shown that Valinomycin forms complexes with the target ions (K^+) that are carried across the solution-membrane boundary and produced a stable Nernstian response that could be evaluated with potentiometry [7], [23].

In this report, we present the development of a new plastic-based ISE incorporating a metalized polyester sheet and CNTs as nanomaterials to transduce the chemical signal of an ISM into an electrical signal. A simple characterization of the PB-ISE was made, and some analytical parameters were optimized.

II. MATERIALS AND METHODS

A. Reagents

Valinomycin (<99%), potassium tetrakis (4-chlorophenyl) borate (KTFPB) with >98% purity, bis(2-ethylhexyl) sebacate with >97% purity (DOS), polyvinyl chloride high molecular weight (PVC), tetrahydrofuran (THF), and sodium dodecylbenzenesulfonate (SDBS) were all purchased from Sigma-Aldrich.

B. CNT Ink preparation

The carbon nanotubes ink (CNT-ink) was prepared by adding CNTs to a 10 mg/mL sodium dodecylbenzene sulfonate (SDBS) aqueous solution, as reported by Novell *et al* [7] and Cui *et al* [24]. A concentration of 3 mg/mL of CNTs was used to achieve ink with optimum stability and adherence [7]. CNTs were successfully dispersed using a bath sonicator (GT SONIC P6, GTSonic, Jeonyoung Co., Ltd. Chungnam, Korea) for 2 h (100 W, frequency of 24 kHz, 80% of amplitude). Secondary reactions were avoided keeping the bath at 4 °C during the sonication. To keep a stabilized CNT-ink was stored in a fridge at 6 °C.

C. CNT ink deposition

CNT ink deposition was carried out on the non-printed side of the recycled MPS from snack packages (Fig. 1a). CNT ink was deposited by the drop-casting technique [25], while the polyester support is heated gradual and controlled [26]. The casting is done by adding cycles of 1 ml of CNT ink onto a 5 x 5 cm MPS surface at 3 different temperatures (80, 100 and 120 °C). The number of cycles applied as a function of the electrical resistance of the final MPS will lead once there are no significant differences in the values of standard deviation. Electrical resistance per square (Ω/□) as well thickness (µm) was measured in a 1 x 1 cm of the conductive MPS.

D. Ion-selective membrane preparation

A potassium ion-selective membrane (K^+-ISM) containing a commercial ionophore was prepared with a cation exchanger (KTFPB), plasticizer (DOS) and PVC. Membranes were prepared by dissolving the ionophore (2 wt%), the cation exchanger (0.5 wt%) and PVC/plasticizer relation (1:3 ratio) with 1 mL of THF by 30 minutes in a sonicator and the cocktail were stored at 4 °C and remained stable for about 2 weeks [7], [20].

E. Ion-selective electrode construction

To make the plastic-based electrodes we used the methodology propose by Novell *et al* [7]. Two plastic masks and a strip of conductive MPS were glued with a laminator. One of the plastic covers had a hole in the top part of the electrode to make the contact between the conductive MPS and the K^+-ISM. 30 µL of the membrane cocktail (ISM) was applied by drop-casting in cycles of 5 µL onto the MPS (just keeping in the orifice of the plastic mask). To make the SC-ISEs, 50 µL of the ISM was deposited by drop-casting onto a commercial SC-ISE followed by solvent evaporation at room temperature as Crespo *et al* [20] reported. Electrodes were conditioned in two potassium solutions (10^{-2} and 10^{-4} M) as Novell *et al* [7] reported.

F. Instrumentation and characterization of ISE

Electromotive forces (EMF) were measured at room temperature (24±4 ºC) using a 6-channel EMF high impedance potentiometer (Lawson Laboratories, Inc.). Measurements were recorded against a double-junction Ag/AgCl/KCl (3 M) reference electrode (6.0729.100, Metrohm AG, Herisau, Switzerland) containing 1M LiAcO as an ionic salt bridge. Calibration curves were constructed by plotting the potential, *EMF/mV*, versus the logarithm of the potassium concentration (Log [K^+]) at room temperature. Potentiometric measurements were performed in stirred solutions for triplicate. Seven ion concentrations from 10^{-7} to 10^{-1} M of K^+ were added successively to increase the EMF decays until obtaining stables values [27].

III. RESULTS AND DISCUSSIONS

Fig. 1 showed a CNT-ink treatment from the initial MPS (Fig. 1b) and the final transformation into a conductive MPS (Fig. 1c). The final MPS was painted with CNT-ink after 6 cycles and it was observed with SEM (Fig. 1d). It's possible to evaluate the interconnected network of CNTs that provides a low electrical resistance in the sample [7], [28]. Fig. 1e showed a decreasing of the MPS resistance after the first CNT-ink deposition. It quickly decays after the application of the first cycle of CNT-ink until the third cycle where the resistance values remained constant. Also, it's possible to observe a dependency of the temperature in the deposition of the CNT-ink onto the MPS.

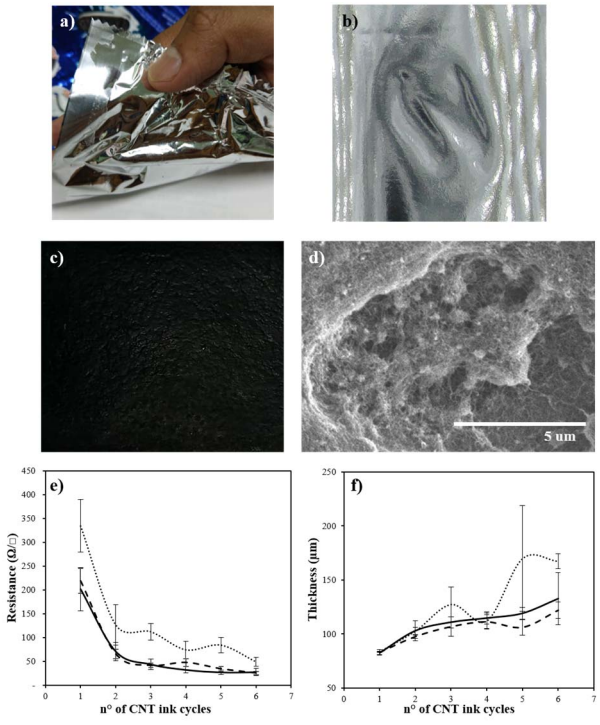

Fig. 1. *(a) Recycled MPS from snack packages. (b) Conversion of MPS into a conductive MPS (c); (c) SEM micrograph of MPS painted with CNT-ink, (d) electrical resistance and (e) thickness of the MPS as a function of the numbers of cycles of CNT-ink at 80 °C (dashed line), 100 °C (solid line) and 120 °C (dotted line).*

Fig. 1d showed a more stable decay in resistance for the MPS at 100°C and an unstable decay in the MPS at 120 °C. Possibly, temperature allows to perm into MPS more easily when CNT ink at 100 °C is applied [26]. However, the authors [7] explain that the values of a few hundred ohms are considered acceptable because the resistance of the system will be controlled by the ISM as other authors reported [24]. As well, Fig. 1e confirms a more stable surface in the MPS at 100 °C (solid line) after the deposition of the CNT-ink. The final conductive MPS is ready to use as a transducer material in an ISE for a potentiometric measure (Fig. 2). For the ISE, a strip of 10 mm by 25 mm is cut and placed between 2 plastic masks as Fig. 2a showed. After a lamination, it's possible to obtain an ISE with a hole where an ISM will be deposited as reported elsewhere [7]. A schematic representation of the potentiometric measurement is shown in Fig. 2b.

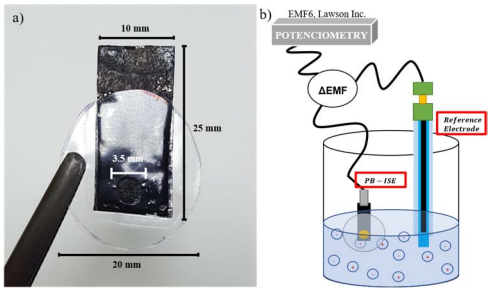

Fig. 2. *(a) The final dimensions of the PB-ISE to use in (b) a potentiometric cell using a reference electrode and the final PB-ISE.*

To assess ISM optimization, a solid contact ion-selective electrode (SC-ISE) was used. The recycled plastic-based electrodes (PB-ISE) were built with the same membrane cocktail, i.e. KTFPB, DOS, and valinomycin. Valinomycin is the ionophore that interacts with potassium dissolved in the solution when different concentrations are added [29]. The PB-ISE allows a drastic reduction in the cost of the sensor and miniaturized the space of working in smaller volumes [8].

TABLE I. ANALYTICAL PERFORMANCE OF THE PB-ISE AND SC-ISE WITH A K^+-ISM

Performance	Electrode	
	Solid Contact (SC)	Plastic-Based (PB)
Slope (mV/dec)	50.15 ± 2.51	52.08 ± 2.36
Liner range [M]	10^{-4} –10^{-1}	10^{-4} – 10^{-1}
LOD [M]	8.01 x 10^{-6}	1.76 x 10^{-5}
Response time (s)	<30	<30

Fig. 3 presents the results for the potentiometric technique. Fig. 3a shows the time trace of the potentiometric response for PB-ISE when the activity of solution adding the primary analyte is increased. Calibration plots for potassium (Fig. 3b) show a near-Nernstian response (52.08 ± 2.36 mV) with a linear range from 10^{-4} to 10^{-1} M, indicating that the membrane works as expected. In all cases, the error bars are small enough, and the standard deviation for the continuous measurement is well below 1 mV. Standard deviations for the SC-ISEs are no-showed but these values are greater than PB-ISEs.

The analytical parameters of the PB-ISE and SC-ISE are reported in Table I. The plasticizer (DOS) not only increases the solubility of the components into the polymeric matrix, but it also improves the detection at lower responses [30]. Whereas the sensitivity is comparable in both cases, the limit of detection (LOD) was decreased by one order of magnitude with SC-ISE giving the same linear range (10^{-4} - 10^{-1} M) for PB-ISE. If we compare the type of ISE, the potassium PB-ISEs shows a sensitivity of 52.08 ± 2.36 mV/dec, which is slightly higher than the value obtained for potassium SC-ISEs (50.15 ± 2.51 mV/dec). The LOD and linear range were comparable in both cases.

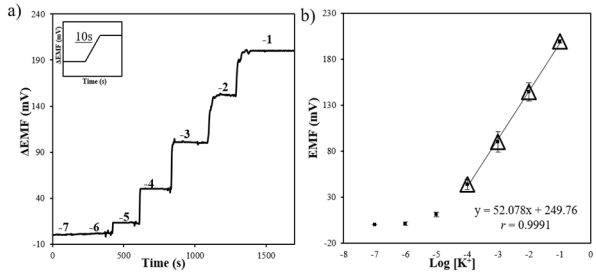

Fig. 3. *Potentiometric response for three different PB-ISEs. In the left (a) is showed the time trace and in the right (b) the corresponding calibration plots after the addition of the potassium. A single addition of the analyte is shown in the inset on the plot (a) with the time response.*

An EMF plot comparing the values obtained for a single calibration curve (potassium concentrations ranging from 10^{-7} M to 10^{-1} M) of both electrodes simultaneously does not show any significant differences (Fig. 4). This is a good agreement with previous work where no significant differences were found between the handmade ISE and conventional ISEs in terms of analytical performances [7]. Therefore, we need to study the accuracy of the technique in more detail as well as the selectivity of the ISE although the results are promising. In a future analysis, we envisage the development of a system where could be integrated into the ISE as a decentralized sensor.

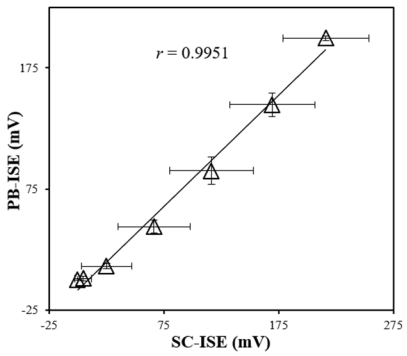

Fig. 4. *EMF plot comparing the values obtained for a single calibration curve using the PB-ISE and SC-ISE for different potassium concentrations.*

IV. CONCLUSIONS

In summary, this work has demonstrated that using an MPS from a plastic waste of food packing to produce a PB-ISE with a near-Nernstian response is possible. All through the combination of a simple platform material and carbon nanotubes is possible to build and produce an ISM based potentiometric sensor with excellent characteristics as simple, rugged, low-cost with good analytical performance. The results suggest that a plastic-based ion-selective electrode shows excellent performance when it is used as potentiometric sensors. Their excellent electrical properties in the new recycled plastic platform and the already demonstrated ideal performance of the CNT as ion-to-electron transducer material make this ISE optimal for ion determinations. Some future work could include an enhancement of the slope for the PB-ISE to achieve more accurate values.

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