Recent Progress in Disposable Ion-selective Sensors for Environmental Applications

Giusy Matzeu[1,a], Claudio Zuliani[1,b] and Dermot Diamond[1,c]

[1]CLARITY Centre for Sensor Web Technologies, National Centre for Sensor Research, Dublin City University, Dublin 9, Ireland

[a] giusy.matzeu2@mail.dcu.ie, [b]claudio.zuliani@dcu.ie, [c]dermot.diamond@dcu.ie

Keywords: Ion Selective Electrodes (ISEs), lead detection, environmental sensors, conducting polymers, water quality

Abstract

Solid-contact Ion Selective Electrodes (SC-ISEs) for the detection of lead have been prepared on screen-printed substrates in order to produce low-cost, disposable sensors for environmental monitoring. The materials used as solid contact layer, the deposition techniques used, and the layer thickness greatly affects the performance of the sensors. Poly(3-octylthiophene-2,5-diyl) (POT) and poly-3,4-ethylenedioxithiophene (PEDOT) have been employed in this investigation. For sensors prepared with POT, the batch reproducibility depends on the amount drop-cast, *i.e.*, thickness. In case of PEDOT which is grown galvanostatically the trend is more complex and batch reproducibility appears to depend on the current density. In the latter case, both the film thickness and both the degree of overoxidation of the polymer appear to influence sensor reproducibility.

Introduction

Heavy metals are an important source of pollution and their monitoring in environmental waters is strictly regulated, as they have been linked to several pathologies. For example, high levels of lead may cause behaviour changes and intelligence impairment in humans [1]. The feasibility of establishing effective distributed sensor networks depends on the availability of sensors that can operate without the need for frequent re-calibration [2,3]. The incorporation of an array of sensors in remote platforms each of which is used once or for a restricted period of days may represent a viable option to achieve long-term deployments [4]. In this regard, disposable Ion-Selective Electrodes (ISEs) prepared on screen printed substrates have been shown to be suitable for the detection of lead at ppb levels in real water samples [4].

In SC-ISEs the internal reference solution can be replaced by solid materials that have both an ionic and electronic mechanism of charge transduction [5-7]. Conducting polymers have been investigated for this purpose previously [5-7]. The solid-contact layer is a critical component of the overall chemical sensing device, as it contributes to the definition of the potential of the sensor and therefore influences the batch reproducibility of the ISEs. Different conducting polymers have been investigated as a possible solid contact layer for ISEs and among these PEDOT and POT are the most encountered. However, preparation of ISEs employs commonly available substrates, *e.g.*, glassy carbon and gold electrodes [5-7] and reproducibility of SC-ISEs is still an outgoing issue especially for trace-analysis [7]. The latter aspect is a significant impediment to more general use of these sensors due to the cost of ownership and practical challenges in the realization of remote sensing networks [1-3]. This manuscript focuses on ways to improve the batch reproducibility of Pb-ISEs, by carefully investigating the role of POT and PEDOT as solid contact. In this regard, it is important to decipher the effect of polymer deposition variables, e.g., the current density, in relation to the final performance of the ISEs rather than following established protocols which have been tested with other substrates and not screen printed electrodes. Finally, the use of screen printed substrates to prepare the Pb-ISE transducers allows sensors to be fabricated with very low production costs.

Experimental

Materials. The carbon ink and the dielectric for the preparation of the screen printed electrodes were obtained from Gwent Inc. 3,4-Ethylenedioxythiophene (97%) (EDOT) and poly(3-octylthiophene-2,5-diyl) (regiorandum) (POT) were purchased from Sigma Aldrich. For the membrane preparation, high molecular weight poly(vinyl chloride) (PVC), bis(2-ethylhexyl) sebacate (DOS, ≥97%), *tert*-butylcalix[4]arene-tetrakis(N,N-dimethylthioacetamide) selectophore (lead ionophore IV), tetrahydrofuran (THF, ≥ 99.5%) of selectophore grade were used without any further purification and they were purchased from Sigma. Sodium tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB) was from Strem Chemicals and chloroform (> 99%) was from Fisher. Standard solutions for the calibration of the ISEs were prepared using lead(II) nitrate of selectophore grade (Sigma).

Preparation of Pb-ISEs. The carbon screen printed electrodes were realized using a DEK 248 printer as reported elsewhere [8]. PEDOT was galvanostatically deposited directly on the carbon electrodes using a CHI760 from a solution of 0.06 M of EDOT in aqueous 0.1 M KCl, which was stirred at 400 rpm. The deposition time was 714 s and the current densities were: 5.15, 6.81, 8.17, 10.6, 16.05, 22.71 and 29.1 μA mm^{-2}. Alternatively, 5.25 or 15.75 or 31.5 or 63 μL of a 2.75 mg mL^{-1} solution of POT in chloroform was drop cast on top of the carbon layer. The EDOT and POT solutions were stirred overnight to facilitate solubilisation. In both cases, the electrodes were left drying overnight following the polymer deposition. A total of 10.5 μL lead sensitive membrane prepared as previously reported [4] was drop cast on top of the conducting polymer layer by multiple additions of 1 μL (3 times), 1.5 μL (twice) 2 μL (once) and finally 2.5 μL (once). The ISEs were conditioned at first in a 10 μM solution of lead nitrate overnight and followed by a 1.0 nM solution of lead nitrate for 24 hours. The pH of both solutions was adjusted to 4 using nitric acid as verified by means of a pH meter. The potentiometric measurements were recorded using the EMF-16 potentiometer from Lawson Labs and a silver/silver chloride (saturated KCl) in a 1.0 M LiOAc salt bridge was used as reference electrode.

Results and Discussion

Fig. 1a and 1b show the SEM images of two electrodes prepared with two different quantities of POT drop-cast on top of the screen printed substrates, respectively 5.25 and 63 μL of a concentration of 2.75 mg ml^{-1}. In Fig. 1a the typical flake structure of the carbon inks and the smooth featureless structure of POT are apparent indicating that not all the carbon screen printed area has been covered by the drop casting. On the other hand, Fig. 1b is completely featureless indicating full coverage of polymer. Indeed, drop casting larger amounts of material progressively increases the coverage of the electrochemical area (not shown). It was noted that after the drop casting on exposed carbon disk the POT layer was thicker at the border between this disk and the dielectric layer surrounding the latter.
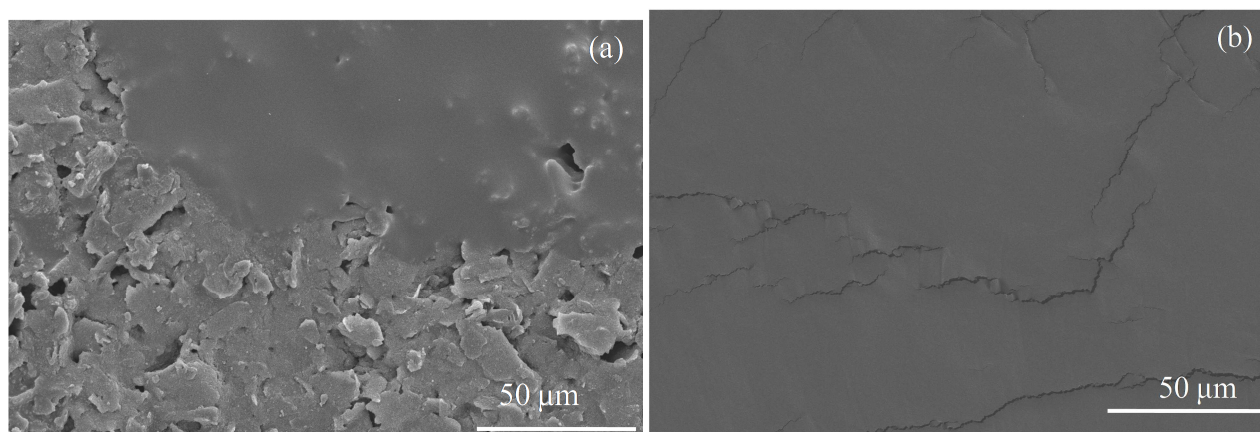

Figure 1. SEM images of the electrodes after drop casting (a) 5.25 μL and (b) 63 μL of 2.75 mg ml^{-1} solution of POT of 2.75 mg ml^{-1} in $CHCl_3$ on top of the screen printed carbon layer. The magnification and accelerating voltage are 1k and 10 kV respectively.

All the sensors prepared with POT as above described show super-Nerstian behaviour. A further study on how the conditioning steps can restore the sensor response to Nerstian behaviour will be undertaken in future. However, it is significant that different quantities of drop cast POT affect the reproducibility of the sensors response. In fact, Fig. 2 shows how the standard deviations of the slope and baseline of the calibration curves depend on the volume of POT drop-cast. Significantly, the two trends, *i.e.*, the one for the baseline and the one for the slope, are different. While the slope is not much affected, the baseline curve appears to go through a minimum. This fact is not fully understood and it needs further investigation.
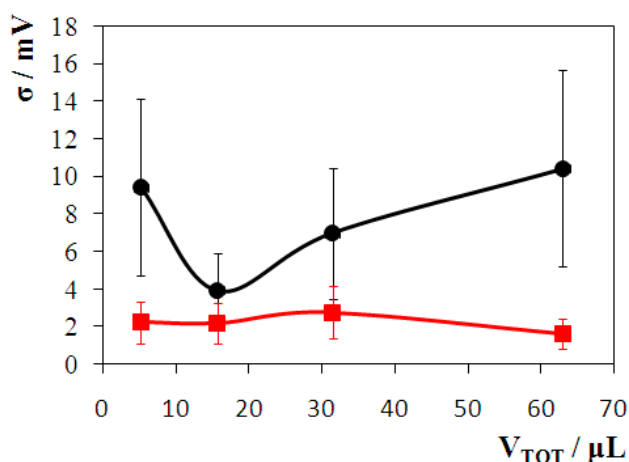

Figure 2. Standard deviation, σ, obtained for the baseline ($\bullet$) and slope ($\blacksquare$) in function of the volume of POT drop cast. Each individual point is the average of 4 sensors.

Fig. 3a and 4a show the SEM images of PEDOT deposited at a current density of 5.15 $\mu A\ mm^{-2}$. It is apparent that at this current density the electrochemical area is not completely covered by the polymer, as the flake-like structures of the carbon ink substrate are visible. At the same time, the chrono-potentiometric curves obtained during the galvanostatic deposition are not completely superimposed. It is likely that this is linked to the PEDOT coverage. Fig. 4a shows that increasing the current density to 8.17 $\mu A\ mm^{-2}$ generates a thicker and more sponge-like PEDOT film which exhibits more effective coverage of the substrate surface. Fig. 4b shows that the chrono-potentiometric curves of the polymer deposition are practically superimposed.
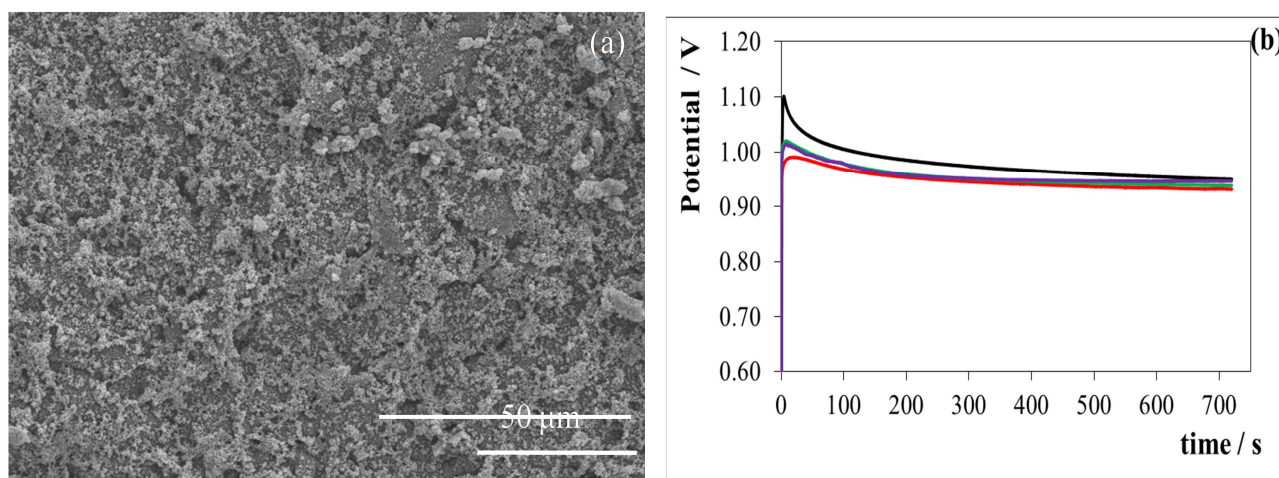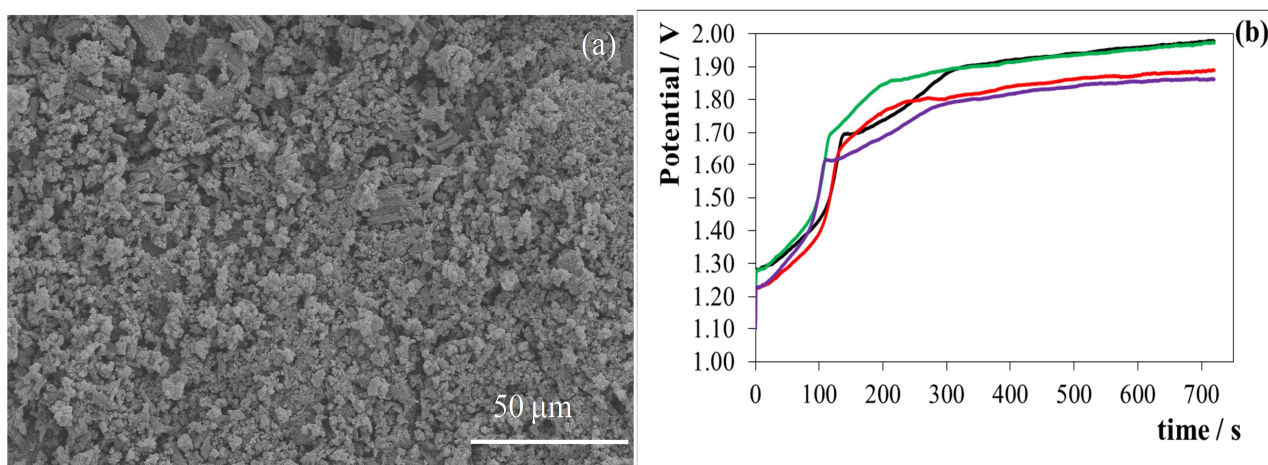

Figure 3. (a) Typical SEM image obtained for the galvanostatic deposition of PEDOT. The magnification and accelerating voltage are 1k and 10 kV respectively. (b) Chrono-potentiometric curves obtained with 4 different carbon screen printed substrates for the galvanostatic deposition of PEDOT. In both cases the current density was 5.15 $\mu A\ mm^{-2}$.
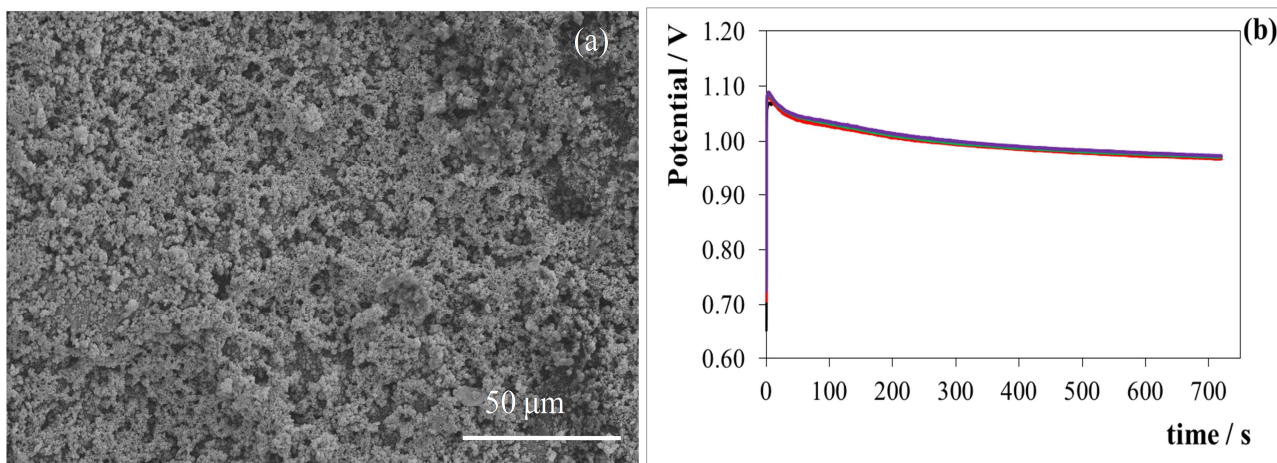
Figure 4. (a) Typical SEM image obtained for the galvanostatic deposition of PEDOT. The magnification and accelerating voltage are 1k and 10 kV respectively. (b) Chrono-potentiometric curves obtained with 4 different carbon screen printed substrates for the galvanostatic deposition of PEDOT. The current density in both cases was 8.17 μA mm^{-2}.

Fig. 5a and 5b show an SEM image and the chrono-potentiometric curve obtained applying a current density of 29.1 μA mm^{-2}. In this case the conformation of the PEDOT layer looks different, with bigger globular structures than the cobweb cover in Fig. 4a. Looking at Fig. 5b it appears that the polymer overoxidation occurs at this current density as potential raised well beyond 1.2 V which according to Du *et al.* [9] is the threshold controlling the overoxidation process. The separation of the potentiometric curves may also indicate that the deposition is less reproducible in this case.

Figure 5. SEM image and (b) chrono-potentiometric curve obtained for the galvanostatic deposition of PEDOT at a current density of 29.1 μA mm^{-2}.

Figure 6 shows the calibration curves obtained with 4 sensors prepared from PEDOT deposition. These curves have a Nernstian behaviour with a slope of 27.5 ± 0.39 mV and a limit of detection of $10^{-6.23}$ M.
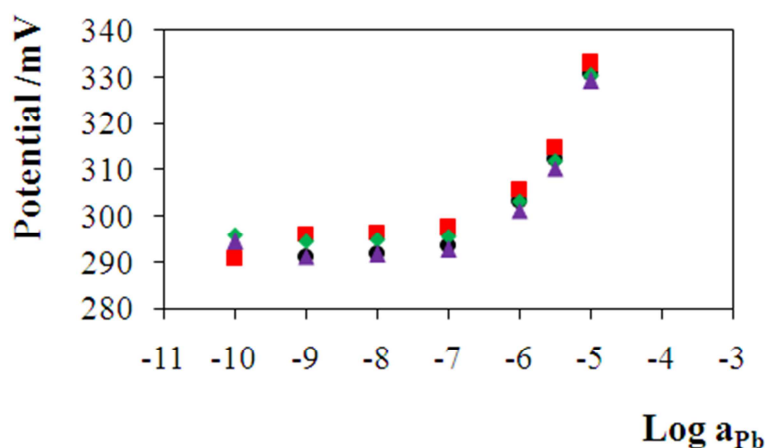
Figure 6. Calibration curves of 4 sensors realized using PEDOT as solid contact. PEDOT was deposited galvanostatically at a current density of 5.15 $\mu A\ mm^{-2}$.

Fig. 7 shows the standard deviations of the slope and baseline of the calibration curves plotted against the current density for the electrodeposition of PEDOT. Comparing to the case of ISEs prepared with POT, the ones prepared using PEDOT show a more complex trend since current density would control not only the thickness of the solid contact but also the "oxidation extent" of this layer. It is significant to note in Fig. 7 a common minimum of the standard deviations for the baseline and slope values obtained at a current density equal to 8.17 $\mu A\ mm^{-2}$. At this value of the current density, a full coverage of the carbon layer with PEDOT is obtained while at lower values of current densities bare areas of carbon are still visible. Therefore, the sub-coverage explains likely the larger standard deviations obtained at current densities lower than 8.17 $\mu A\ mm^{-2}$. Interestingly, an abrupt increase of the standard deviations is observed for the current immediately next to the minimum. In fact, at this current density, *i.e.*, 10.6 $\mu A\ mm^{-2}$ the experimental potential observed during PEDOT deposition is below 1.1 V and an increase of the current density should cause only an increase of the thickness of the PEDOT layer [11]. A further increase in the current density leads to a reduction in the standard deviation which finally levels off. Significantly, the last two points, *i.e.*, 22.71 and 29.1 $\mu A\ mm^{-2}$ correspond to a situation at which the polymer has been increasingly over-oxidized.
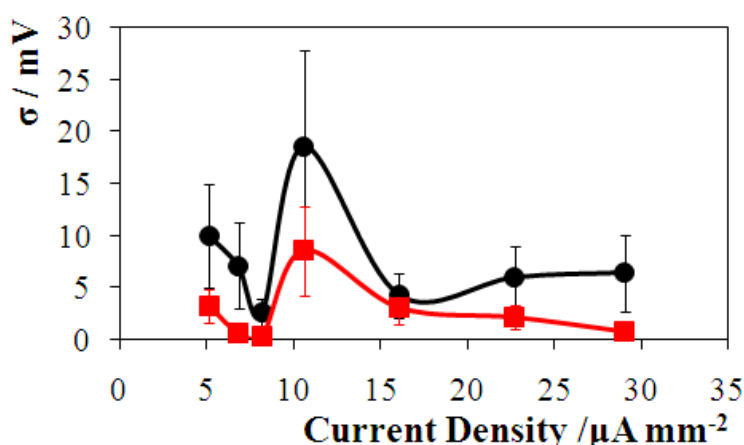
Figure 7. Standard deviation, σ, obtained for the baseline ($\bullet$) and slope ($\blacksquare$) in function of the current density for the electrodeposition of PEDOT. Each individual point is the average of 4 sensors.

Conclusions

These results show how PEDOT and POT affect the performances of Pb-ISEs. Care was taken in tackling the batch reproducibility of the sensors calibration curve by optimizing the solid contact. It is shown that by tuning the current density for electropolymerization of PEDOT, on one hand, and the drop cast volume of POT, on the other hand, the batch reproducibility of these sensors can be significantly improved. The use of screen printed substrates for the preparation of the ISEs and the minimization of the analytical deviations intra-batch in the calibration curves of the sensors may allow the use of SC-ISEs as low-cost environmental sensors with great potential for their establishment in deployed sensing platforms. Other types of solid contacts are currently under investigation to understand if sensors reproducibility can be further improved compared to results here presented.

Acknowledgments

References

[1] C. Zuliani, D. Diamond, Opportunities and Challenges of using Ion-Selective Electrodes in Environmental Monitoring and Wearable Sensors, Electrochim. Acta. (2012), In Press.

[2] D. Diamond, S. Coyle, S. Scarmagnani, J. Hayes, Wireless Sensor Networks and Chemo-/Biosensing, Chemical Reviews. 108 (2007) 652.

[3] R. Byrne, D. Diamond, Chemo/bio-sensor networks, Nature Materials. 5 (2006) 421.

[4] S. Anastasova, A. Radu, G. Matzeu, C. Zuliani, U. Mattinen, J. Bobacka, D. Diamond, Disposable solid-contact ion-selective electrodes for environmental monitoring of lead with ppb limit-of-detection, Electrochim. Acta. 73 (2012) 93-97.

[5] J. Bobacka, A. Ivaska, Chemical Sensors based on conducting polymers, in: S. Cosnier and A. Karyakin (Ed.), Electropolymerization. Concepts, Materials, and Applications, Wiley-VCH, Weinheim, Germany, 2010, pp. 173.

[6] J. Bobacka, A. Ivaska, Electrochemical Sensor Analysis, in: Alegret, S., Merkoçi, A. (Ed.), Comprehensive Analytical Chemistry, Elsevier, 2007, pp. 73.

[7] J. Bobacka, A. Ivaska, A. Lewenstam, Potentiometric Ion Sensors, Chemical Reviews. 108 (2008) 329.

[8] G. Matzeu, C. Zuliani, D. Orpen, D. Diamond, (in preparation).

[9] X. Du, Z. Wang, Effects of polymerization potential on the properties of electrosynthesized PEDOT films, Electrochim. Acta. 48 (2003) 1713-1717.

[10] B. Paczosa-Bator, J. Peltonen, J. Bobacka, A. Lewenstam, Influence of morphology and topography on potentiometric response of magnesium and calcium sensitive PEDOT films doped with adenosine triphosphate (ATP), Anal. Chim. Acta. 555 (2006) 118-127.

[11] J. Bobacka, A. Lewenstam, A. Ivaska, Electrochemical impedance spectroscopy of oxidized poly(3,4-ethylenedioxythiophene) film electrodes in aqueous solutions, J Electroanal Chem. 489 (2000) 17-27.

Adaptive, Active and Multifunctional Smart Materials Systems

Recent Progress in Disposable Ion-Selective Sensors for Environmental Applications