

Review

Application of Photocured Polymer Ion Selective Membranes for Solid-State Chemical Sensors

Natalia Abramova ^{1,2,†,*} and Andrey Bratov ^{1,†}

¹ BioMEMS Group, Instituto de Microelectronica de Barcelona, Centro Nacional de Microelectrónica (CSIC), Campus U.A.B., Bellaterra, Barcelona 08193, Spain; E-Mail: andrei.bratov@imb-cnm.csic.es

² Lab. Artificial Sensors Syst., ITMO University, Kronverskiy pr. 49, St. Petersburg 197101, Russia

† These authors contributed equally to this work.

* Author to whom correspondence should be addressed; E-Mail: natalia.abramova@imb-cnm.csic.es; Tel.: +34-935-947-700 (ext. 2209); Fax: +34-935-800-267.

Academic Editor: Igor Medintz

Received: 27 March 2015 / Accepted: 22 May 2015 / Published: 2 June 2015

Abstract: Application of conducting polymers with additional functional groups for a solid contact formation and photocurable membranes as sensitive elements of solid-state chemical sensors is discussed. Problems associated with application of UV-curable polymers for sensors are analyzed. A method of sensor fabrication using copolymerized conductive layer and sensitive membrane is presented and the proof of concept is confirmed by two examples of solid-contact electrodes for Ca ions and pH.

Keywords: solid-state ion-to-electron transduction; conducting polymers; photocurable membranes; ion-selective electrodes

1. Introduction

The history of solid-state chemical sensors is a history of attempts to find materials and technological process that permit to obtain stable signal on miniaturized devices fabricated by mass production technologies. Here we may speak not only about a very large group of ion-selective electrodes (ISE) with inner solid contact and coated wire electrodes (CWE) but also sensors based on field effect transducers, like ion-selective field effect transistors (ISFETs), light addressable potentiometric sensors (LAPS) and electrolyte-insulator-semiconductor (EIS) capacitances. In the case

of electrodes the major challenge was to obtain a fast and thermodynamically reversible ion to electron transduction system that may fix the potential at the solid-contact/ membrane interface [1]. For field-effect sensors it was necessary to find materials with very strong adhesion to fix an ion-selective membrane on a solid substrate by methods that are compatible with microelectronic technology [2].

Most of the solid-type ion sensors based on field effect devices with a silicon oxide or silicon nitride upper layer have used PVC as a membrane polymer matrix. One of the primary causes of failure in these sensors is penetration of water through the membrane. Due to the water uptake, thin aqueous layers or pools of water can be formed at the membrane/electrode interface in potentiometric solid-contact ion sensors resulting in potential instability and poor membrane adhesion to the solid contact [3].

Today we can say that using conducting polymers as intermediate transduction layer for solid-state electrodes construction is one of the best solutions [4,5]. On the other hand, application of photocurable polymers as ion-selective membrane matrices for semiconductor based sensors, like ISFETs, ChemFETs and LAPS, as well as for their encapsulation is also very successful. So, may be it is possible to resolve the contact problems of solid state ISE by combine these two classes of materials? Can we use for solid contact conducting polymers with functional groups able to be co-polymerized with photocurable membranes as sensitive elements? This assumption is confirmed by the latest publications in the field [6–8]. The first attempt to obtain a solid-state ion sensor with acrylate-based membrane on a gold electrode modified with a monolayer combining both the ferrocene- and acrylate- terminated thiols to enhance the adhesion and prevent water layer formation was reported in [9], but this approach did not undergo further evolution.

It may be possible to chemically bind the conducting polymer layer and acrylate based polymer membrane may be possible by modifying the redox polymer with acrylate groups that participate in photopolymerisation reaction. Introduction of photopatterning groups in polyanilines (PANIs) [8] or polythiophenes [7] has led to improvements in surface hydrophilicity, biocompatibility, and adhesion properties of these materials. Improvements of this type allow the polymer films to be used in many potential applications by combining the appropriate functional groups with a conjugated polymer backbone [6].

Photocurable polymers as an alternative material for membrane matrices for ISFETs, solid contact electrode (SCE) and coated wire electrode were introduced by different research groups in the middle of 1980s and early 1990s. Bibliographic data on application of photocurable polymers for chemical and ion sensor development are summarized in [10]. The use of photocured polymeric systems permits to employ a standard photolithographic process, which reduces significantly the time of membrane deposition and manual work required for it, items that are important for sensor mass production. At the same time conducting polymers with photopolymerizable groups applied by using of thin- and thick-films microfabrication technologies can result in cheap, mass-produced sensor arrays that can be integrated with control electronic in a straightforward way [11].

Another positive feature of these two classes of organic polymers is the opportunity to obtain an ISE membrane chemically attached to solid support and without leaching of its main components (ionophore, lipophilic additives, and plasticizer). This approach was applied some years ago by the group of D. Reinhoudt for modified polysiloxanes membranes [12,13] and by D.Harrison and co-workers [14] for PVC. However, the synthesis of these copolymerized compounds seems to require much effort.

In consideration of proposed idea the aim of this mini-review is to discuss some problems that may arise in the case of photocurable membranes application and present the proof of concept and some examples of solid-contact electrodes with copolymerized conductive layer and sensitive membrane.

2. Possible Problems of Photocurable Polymers as Membrane Matrices

2.1. Use of Porphyrins and Plasticizers with Nitro(–NO₂) Functional Groups

One of the problems related to photocurable polymer membrane matrices is the impossibility of using some plasticizers or ionophores especially in the case of radical initiation of polymerisation because they can inhibit this type of reaction. No polymerisation occurs when 2-nitrophenyl octyl ether (NPOE) or 4-nitrophenyl phenyl ether (NPPE), two most common plasticizer for bivalent ions like Ca or Mg, are used in membrane compositions [15]. In this case they should be replaced by some other plasticizer, like octyl [2-(trifluoromethyl)phenyl] ether.

The presence of porphyrines and their derivatives, well known as a photosensitizers due to efficient photoinduced reactions with molecular oxygen [16], acting as ionophores in many anion selective membrane compositions, completely inhibits the photopolymerisation process too. This problem may be partly resolved by changing the type of photopolymerisation mechanism from radical to cationic [17,18] that is less susceptible to inhibition by these substances. As a photoinitiator of cationic polymerisation process a mixture of quinone derivatives and phenyliodonium salt is used. It must be taken into consideration that introduction of photoinitiators may affect analytical parameters of sensors. It is well known that a photoinitiator is not totally consumed in the reaction [19] and though its concentration in the membranes is not very high it is comparable with the concentration of an ionophore and lipophilic additives (1%–2% w/w). This may result in that the products of fragmentation and unreacted substances alter ion-selective properties of the resulting membranes. Usually the selectivity of membranes that were cured via cationic means is not very high [10].

2.2. Photobleaching of Membrane Components

Another problem that may arise in the case of photocurable polymer membranes is a photobleaching of the membrane components upon extended UV exposure during the polymerization processes. It is known that the stability of tetraphenylborate ion is limited, especially in the presence of acids and oxidizing agents and under UV illumination [20]. Decomposition of tetraphenylborate derivatives takes place with the consumption of a proton, giving as a result neutral products. This means that the final concentration of tetrakis(*p*-chlorophenyl)borate ion, that is normally used in ion selective membrane formulations in order to reduce the electrical resistance of the membrane and to obtain better selectivity, may depend on UV exposure time. The extent of interference of highly lipophilic anions (e.g., CNS[–]) in solution may be used as an indicator for the K-TpCIPB content in the membrane. In Figure 1 calibration curves of sensors with membranes containing plasticizer and K-TpCIPB and polymerized with different exposure times are presented along with the calibration curve for membrane without lipophilic anion [2]. From this figure it is clear that with the increase of the exposure time the cationic response of the membrane switches to anionic at much lower concentrations of KCNS due to the lower concentration of K-TpCIPB.

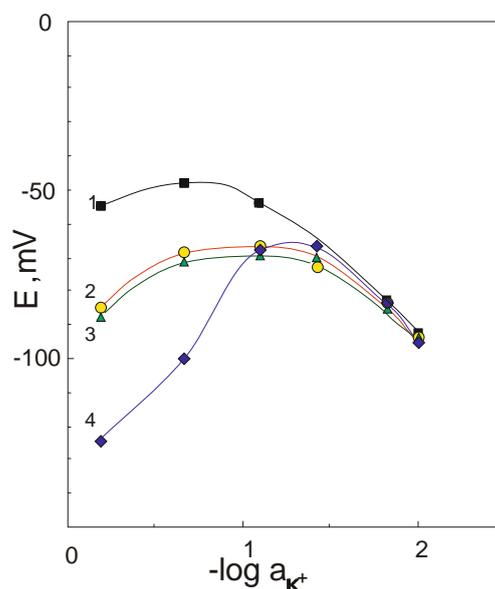


Figure 1. Calibration curves for polyurethane membranes containing K-TpCIPB and a plasticizer in solutions of highly lipophilic anion (KCNS). The membranes differ in the UV exposure time used for polymerization: **1**—2 min of irradiation; **2**—10 min; **3**—20 min; **4**—membrane without K-TpCIPB and with 2 min of irradiation. Adapted from [2].

It must be taken into account that not only lipophilic additives but ionophore as well may be affected by photochemical reactions occurring during UV irradiation of the membrane matrix. It was shown in the case of pH selective photocurable membrane [21] that the optimal ionophore/lipophilic salt ratio differs significantly from that theoretically recommended for this type of ion-selective membranes [22]. In this work tertiary amines (NR_3), where R is $\text{CH}_3(\text{CH}_2)_{11}$, were used as H^+ -selective ionophores. These compounds are also widely employed as donors of protons in reactions of photopolymerization. At the same time in the membrane are present p-tetrachlorophenylborate anions $(\text{p-CIPh})_4\text{B}^-$, which readily undergo photolysis, and the photoinitiator of radical polymerization (2,2'-dymetoxyphenylacetophenone). As a result, the process of irradiation leads to the formation of a radical pair between $\text{R}_3\text{N}^{\cdot+}$ and $\cdot\text{B}^-(\text{p-CIPh})_4$. This initially formed radical pair has a very short lifetime but may participate in different reactions of recombination, cleavage and propagation. As a consequence of these reactions real concentrations of the ionophore and lipophilic salt, determining the selectivity of the membrane, are different from the original, introduced into the membrane composition.

2.3. Copolymerisable Plasticizers

One of the advantages of photocurable membranes is the facility to obtain ‘mixed’ polymers by introducing different acrylated monomers that can be co polymerised to form membrane polymer matrix with required properties. Attempts to prevent the leaching of ion active components from thin (30–100 μm) membranes began with the synthesis of a so called copolymerizable plasticizers [14]. More lately ‘plasticizer-free’ [23] or ‘self-plasticizing’ [24] ion-selective membranes have been introduced. This type of ‘self-plasticizing’ polymer matrices, that were found to be compatible with most of commercially available ionophores, can be produced by free-radical polymerization, both

cationic and UV-induced, using different types of acrylate- or methacrylate-based oligomers. With these polymers sensors for potassium, sodium, chloride, calcium and pH were fabricated entirely by photocure procedures [25–27].

It must be noted that the absence of a free plasticizer within the membrane matrix may cause two problems. Firstly, the solubility of an ionophore and lipophilic additives in the membrane mixture will be decreased, which may seriously affect the sensor parameters like sensitivity, selectivity and limit of detection. Secondly, this will affect the mobility of charged species within the membrane phase which will result in very high membrane impedance (50–200 M Ω) [28,29].

3. Solid Contact Electrodes Based on Copolymerized Conducting Polymer and Photocurable Membranes

As we mentioned earlier in the text, introducing of photopatterning groups into conductive polymer backbone may permit to copolymerize this material with the ion-selective membrane matrix during UV-polymerization step. Here we presented the proof of concept of a solid contact sensor based on conducting polymers with polymerizable functional groups as a solid contact and photocurable membranes as a sensitive element. Two examples of solid contact electrodes presented below used a monomer *N*-phenylethylenediamine methacrylamide (NPEDMA) to form a conductive layer. Resulting polymer contains both an aniline and a methacrylamide group, capable of polymerisation by free radical methods. The monomer may also be polymerised electrochemically onto a suitable electrode, giving a conductive polymer surface which can be modified on the next step by any of photochemical reactions of methacrylate moieties. Another possibility of polymerization is via chemical oxidative method with ammonium persulfate.

As a membrane matrices we have used Ca-selective photocurable membrane with mixture of free (dioctyl sebacate, DOS) and copolymerisable (hexafluorobutyl acrylate, HFBuA) plasticizers and pH- selective membrane with copolymerizable plasticizer di-(*n*-hexyl)-itaconate (DHI), presented earlier [21,29].

More detailed information on the electrode construction and characterisation will be presented in a forthcoming publication [30]. Briefly, electrodeposition was performed with a 0.05 M water solution of monomer NPEDMA and 0.1 M 4-dodecylbenzenesulfonic acid (DBS), which was used as counterion. Thin film of the polymer (24 μm , as determined by confocal microscopy) was synthesized using a potentiodynamic method by cycling the potential from -0.5 V to 0.8 V *versus* Pt during 100 repeated cycles. We used a three-electrode cell configuration containing 24 mL of electrolyte solution, with a Pt foil as counter electrode and Pt wire as quasi-reference electrode. Chemical oxidative method was used as presented in [8]. In both cases thin film gold electrodes deposited by an e-beam on a Cyclic Olefin Copolymer (COP) substrate were used for sensor construction. Obtained polyNPEDMA films were characterized by cyclic voltammetry, electrochemical impedance, Fourier transform infrared attenuated total reflection (FTIR-ATR) analysis and contact angle measurements with results to be presented in [30].

Schematically electrode design is presented in Figure 2. Calibration curves for Ca-selective electrode and pH-electrodes are given in Figures 3 and 4, respectively.

In the case of Ca sensitive membrane calibrations curves were obtained in solutions with 0.1 M NaCl and 0.1 M KCl as a background. For pH membrane we used 0.05 M TRIS and changed the pH values by 6 M HCl. A double-junction Ag/AgCl reference electrode (Orion 90-02) was used as an external electrode with a 0.1 M solution of lithium acetate as a salt bridge in both cases. The standard electrode potentials, E^0 , of three identical electrodes were 329.1 ± 1.9 mV and 368.5 ± 2.1 mV, respectively for calcium and pH sensors, which may be regarded as a good reproducibility among those reported for solid contact electrodes with conducting polymers [31]. From the insert in Figure 3 we can see that the response time and potential stability of the solid contact sensor are the same order of magnitude as for the last examples of all-solid-state electrochemical platform based on conductive polymers, submitted recently [32].

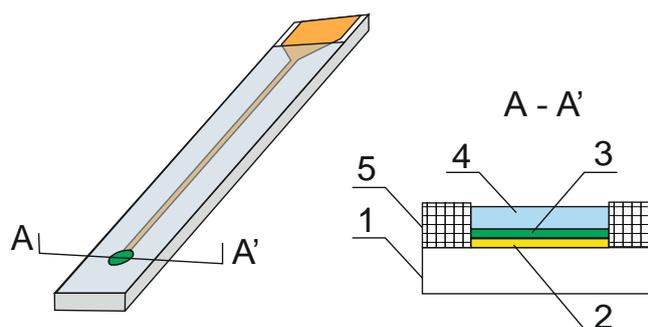


Figure 2. Solid contact electrode design and cross-section of the electrode area. **1**—COP substrate; **2**—thin film gold layer; **3**—poly NPEDMA conductive polymer layer; **4**—polyurethane diacrylate based ion selective membrane; **5**—encapsulating layer based on an acrylic pressure sensitive adhesive (PSA).

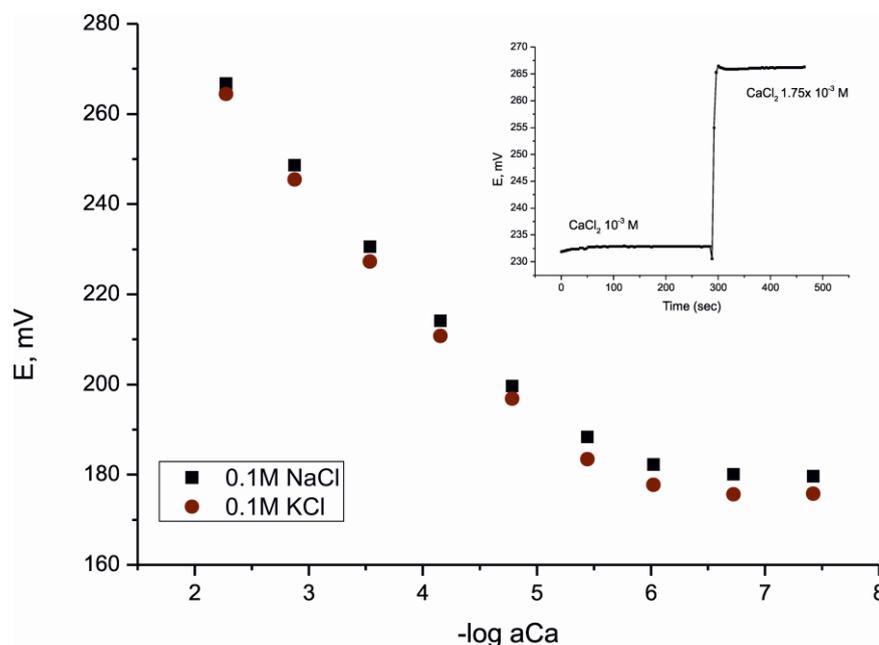


Figure 3. Calibration curves for Ca-selective electrodes (mean values for 3 sensors) in solutions with 0.1 M NaCl and 0.1 M KCl as a background. Insert: Response time of the electrodes in pure solutions of CaCl_2 .

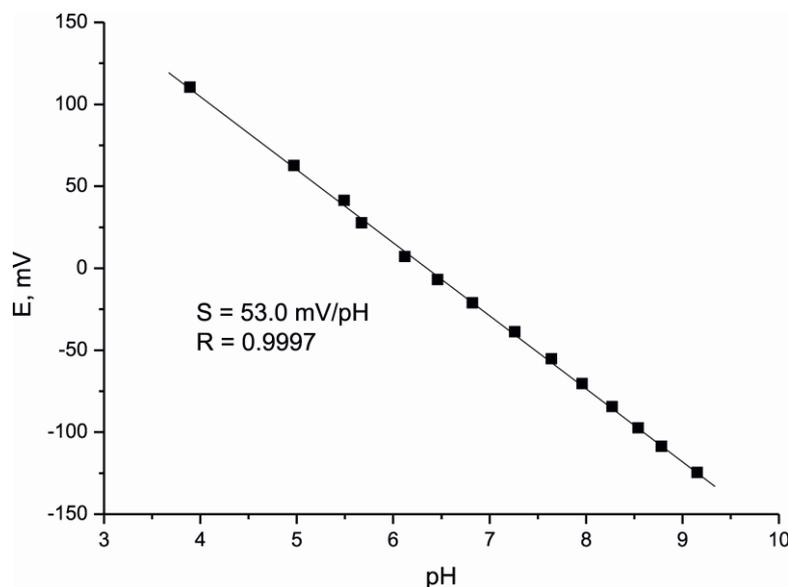


Figure 4. Calibration curve for pH electrode (mean of the values for 3 sensors).

To test for a possible presence of an aqueous layer between the polymer membrane and the solid contact we used a quality control criteria introduced by E. Pretsch and coworkers [33] in which the potential drifts of studied electrodes in solutions of primary and interfering ions were recorded during more than 24 h. Results of this potentiometric aqueous layer test are presented in Figure 5 showing quick recovery of the sensor potential. This manifests that no aqueous layer is formed at the membrane interface with the contact layer.

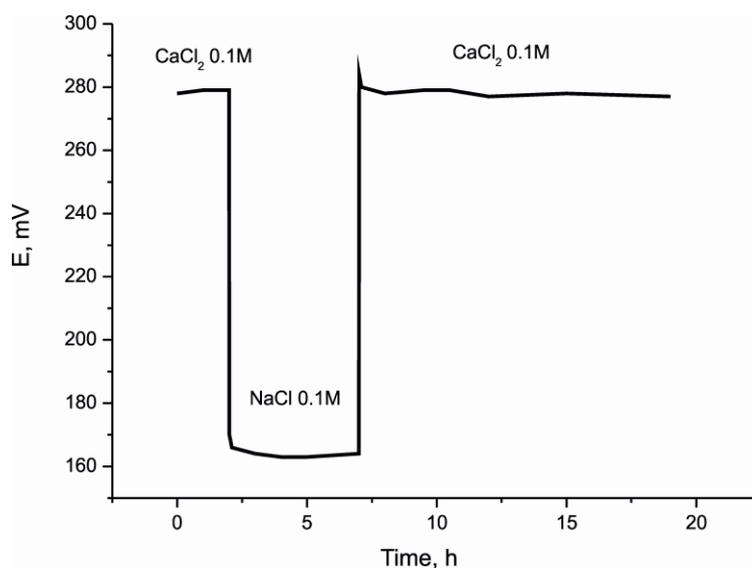


Figure 5. Aqueous layer test in 0.1 M primary ion (Ca^{2+}) and interfering ion (Na^+) solutions.

4. Conclusions

In this review, basing on our previous experience in the development of ion selective membranes for microelectronic devices, some problems that may arise in the case of application of photocurable membranes are discussed. Along with this, a new method of a solid contact ion sensor fabrication is

presented based on a copolymerization between the layer of conductive polymer with polymerizable functional groups and photocurable ion selective membrane as a sensitive element. The concept has been proofed by preliminary experimental results obtained on thus fabricated pH- and Ca²⁺- ion sensors. Taking to account the growing interest in the development of cheap, mass-produced sensors and sensors arrays combined together with microactuators (valve, pumps, channels, *etc.*) and micro flow cells, the concept presented here may be useful for construction of analytical systems of the next generation, like micro total analysis system (μ -TAS) or lab-on-a-chip devices.

Acknowledgments

Authors acknowledge financial support from Spanish Ministry of Economy and Competitiveness (projects IPT-2011-1055-900000 and CTQ2011-29163-C03-02).

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Bobacka, J.; Ivaska, A.; Lewenstam, A. Potentiometric ion sensors. *Chem. Rev.* **2008**, *108*, 329–351.
2. Abramova, N.; Bratov, A. Photocurable polymers for ion selective field effect transistors. 20 years of application. *Sensors* **2009**, *9*, 7097–7110.
3. He, N.; Lindfors, T. Determination of Water Uptake of Polymeric Ion-Selective Membranes with the Coulometric Karl Fischer and FT-IR-Attenuated Total Reflection Techniques. *Anal. Chem.* **2013**, *85*, 1006–1012.
4. Lindfors, T.; Szuecs, J.; Sundfors, F.; Gyuresanyi, R.E. Polyaniline Nanoparticle-Based Solid-Contact Silicone Rubber Ion-Selective Electrodes for Ultratrace Measurements. *Anal. Chem.* **2010**, *82*, 9425–9432.
5. Veder, J.-P.; de Marco, R.; Clarke, G.; Chester, R.; Nelson, A.; Prince, K.; Pretsch, E.; Bakkert, E. Elimination of undesirable water layers in solid-contact polymeric ion-selective electrodes. *Anal. Chem.* **2008**, *80*, 6731–6740.
6. Ivanova-Mitseva, P.K.; Fragkou, V.; Lakshmi, D.; Whitcombe, M.J.; Davis, F.; Guerreiro, A.; Crayston, J.A.; Ivanova, D.K.; Mitsev, P.A.; Piletska, E.V.; *et al.* Conjugated Polymers with Pendant Iniferter Units: Versatile Materials for Grafting. *Macromolecules* **2011**, *44*, 1856–1865.
7. Kim, J.; You, J.; Kim, E. Flexible Conductive Polymer Patterns from Vapor Polymerizable and Photo-Cross-Linkable EDOT. *Macromolecules* **2010**, *43*, 2322–2327.
8. Lakshmi, D.; Whitcombe, M.J.; Chianella, I.; Piletska, E.V.; Guerreiro, A.; Subrahmanyam, S.; Davis, F.; Brito, P.S.; Fowler, S.A.; Piletsky, S.A. Chimeric polymers formed from a monomer capable of free radical, oxidative and electrochemical polymerisation. *Chem. Commun.* **2009**, *19*, 2759–2761.
9. Grygolowicz-Pawlak, E.; Palys, B.; Biesiada, K.; Olszyna, A.R.; Malinowska, E. Covalent binding of sensor phases—A recipe for stable potentials of solid-state ion-selective sensors. *Anal. Chim. Acta* **2008**, *625*, 137–144.

10. Abramova, N.; Bratov, A. Photocurable polymer membrane ion sensor and their application for multicomponent analysis. In *Multisensor Systems for Chemical Analysis*; Lvova, L., Kirsanov, D., di Natale, C., Legin, A., Eds.; Pan Stanford Publishing Pte. Ltd.: Singapore, Singapore, 2014; pp. 41–68.
11. Lindner, E.; Gyurcsanyi, R.E. Quality control criteria for solid-contact, solvent polymeric membrane ion-selective electrodes. *J. Solid State Electrochem.* **2009**, *13*, 51–68.
12. Verkerk, U.H.; van den Vlekkert, H.H.; Reinhoudt, D.N.; Engbersen, J.; Honig, G.; Holterman, H. Development of chemically modified ISFETs as durable sensors for continuous flow measurements. *Sens. Actuators B Chem.* **1993**, *13*, 221–225.
13. Reinhoudt, D.N.; Engbersen, J.; Brzozka, Z.; van den Vlekkert, H.H.; Honig, G.; Holterman, H.; Verkerk, U. Development of durable K⁺-selective chemically modified field effect transistor with functionalized polysiloxane membranes. *Anal. Chem.* **1994**, *66*, 3618–3623.
14. Harrison, D.J.; Teclerian, A.; Cunningham, L.L. Photopolymerization of plasticizers in ion-sensitive membranes of solid-state sensors. *Anal. Chem.* **1989**, *61*, 246–251.
15. Cardwell, T.J.; Cattrall, R.W.; Iles, P.J.; Hamilton, I.C. Photocured polymers in ion-selective membranes. 2. A calcium electrode for flow-injection analysis. *Anal. Chim. Acta* **1985**, *177*, 239–242.
16. Arnaut, L.G. Design of porphyrin-based photosensitizers for photodynamic therapy. In *Advances in Inorganic Chemistry, Vol 63: Inorganic Photochemistry*; VanEldik, R., Stochel, G., Eds.; Academic Press: Waltham, MA, USA, 2011; Volume 63, pp. 187–233.
17. Alexander, P.W.; Dimitrakopoulos, T.; Hibbert, D.B. A Photo Cured Coated Wire Calcium Ion Selective Electrode for Use in Flow Injection Potentiometry. *Talanta* **1997**, *44*, 1397–1405.
18. Dumschat, C.; Fromer, R.; Rautschek, H.; Muller, H.; Timpe, H.-J. Photolithographically patternable nitrate-sensitive acrylate-based membrane. *Anal. Chim. Acta* **1991**, *243*, 179–182.
19. Pappas, S.P. *Radiation Curing: Science and Technology*; Plenum Press: New York, NY, USA, 1992.
20. Rosatzin, T.; Bakker, E.; Suzuki, K.; Simon, W. Lipophilic and immobilized anionic additives in solvent polymeric membranes of cation-selective chemical sensors. *Anal. Chim. Acta* **1993**, *280*, 197–208.
21. Abramova, N.; Bratov, A. Photocurable pH-sensitive membrane for ion-selective field effect transistors. *Talanta* **2010**, *81*, 208–212.
22. Bakker, E.; Xu, A.; Pretsch, E. Optimum composition of neutral carrier based pH electrodes. *Anal. Chim. Acta* **1994**, *295*, 253–262.
23. Van den Berg, A.; Verney-Norberg, E.; Grisel, A. An ISFET-based calcium sensor using photopolymerized polysiloxane membrane. *Sens. Actuators B Chem.* **1991**, *4*, 235–238.
24. Van der Wal, P.D.; van den Berg, A.; de Rooij, N.F. Universal approach for the fabrication of Ca²⁺, K⁺ and NO³⁻ sensitive membrane-ISFETs. *Sens. Actuators B Chem.* **1994**, *18*, 200–207.
25. Heng, L.Y.; Hall, E.A.H. Producing ‘self-plasticizing’ ion-selective membranes. *Anal. Chem.* **2000**, *72*, 42–51.
26. Heng, L.Y.; Hall, E.A.H. Assessing a photocured self-plasticised acrylic membrane recipe for Na⁺ and K⁺ ion selective electrodes. *Anal. Chim. Acta* **2001**, *443*, 25–40.

27. Abramova, N.; Ipatov, A.; Levichev, S.; Bratov, A. Integrated multi-sensor chip with photocured polymer membranes containing copolymerised plasticizer for direct pH, potassium, sodium and chloride ions determination in blood serum. *Talanta* **2009**, *79*, 984–989.
28. Bratov, A.; Abramova, N.; Dominguez, C. Investigation of chloride sensitive ISFETs with different membrane compositions suitable for medical applications. *Anal. Chim. Acta* **2004**, *514*, 99–106.
29. Abramova, N.; Bratov, A.; Ipatov, A.; Levichev, S.; Aris, A.; Rodriguez, E. New flow-through analytical system based on ion-selective field effect transistors with optimised calcium selective photocurable membrane for bovine serum analysis. *Talanta* **2013**, *113*, 31–35.
30. Moral, J.; Abramova, N.; Bratov, A. Solid contact electrodes with copolymerized conductive layer and membrane matrix. *Talanta* **2015**, submitted.
31. Lindfors, T.; Hoefler, L.; Jagerszki, G.; Gyurcsanyi, R.E. Hyphenated FT-IR-Attenuated Total Reflection and Electrochemical Impedance Spectroscopy Technique to Study the Water Uptake and Potential Stability of Polymeric Solid-Contact Ion-Selective Electrodes. *Anal. Chem.* **2011**, *83*, 4902–4908.
32. Mousavi, Z.; Granholm, K.; Sokalski, T.; Lewenstam, A. All-solid-state electrochemical platform for potentiometric measurements. *Sens. Actuators B Chem.* **2015**, *207*, 895–899.
33. Fibbioli, M.; Morf, W.E.; Badertscher, M.; de Rooij, N.F.; Pretsch, E. Potential drifts of solid-contacted ion-selective electrodes due to zero-current ion fluxes through the sensor membrane. *Electroanalysis* **2000**, *12*, 1286–1292.

© 2015 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).