Chapter 16
Components of All-Solid-State Ion-Selective Electrodes (AS-ISEs)

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16.1 Introduction

An electrochemical sensor is a qualitative and quantitative device that converts a chemical signal to a measurable electrical signal (Yogeswaran and Shen-Ming 2008). Electrochemical sensors can be divided into three classes: potentiometric, amperometric, and conductometric (Stradiotto et al. 2003). A potentiometric sensor measures an electrical potential when no current is present, while an amperometric sensor produces current when a potential is applied between two electrodes. A conductometric sensor assesses conductivity by measuring the electrical resistance of a sample solution. Ion-selective electrodes (ISEs) are potentiometric ion sensors and a subgroup of electrochemical sensors; they are widely used in various fields of biomedical, environmental, and chemical analysis, and physiological sensing (Bobacka et al. 2003; Bakker et al. 2008; Hu et al. 2016). ISEs are classified into three groups, depending on the nature of the membrane material: glass, polymeric or liquid, and crystal or solid (Fig. 16.1) (Faridbod et al. 2007).

All-solid-state ion-selective electrodes (AS-ISEs) are solid-based selective membrane electrodes that convert the activity of a specific ion to a measurable electrical signal without an internal filling solution – a liquid electrolyte that separates the sensing membrane from the inner reference electrode (Bobacka 2006; Bratovčić et al. 2009; Faridbod et al. 2008). Measuring voltage potential requires two electrodes: a reference electrode and a sensing electrode. The reference electrode

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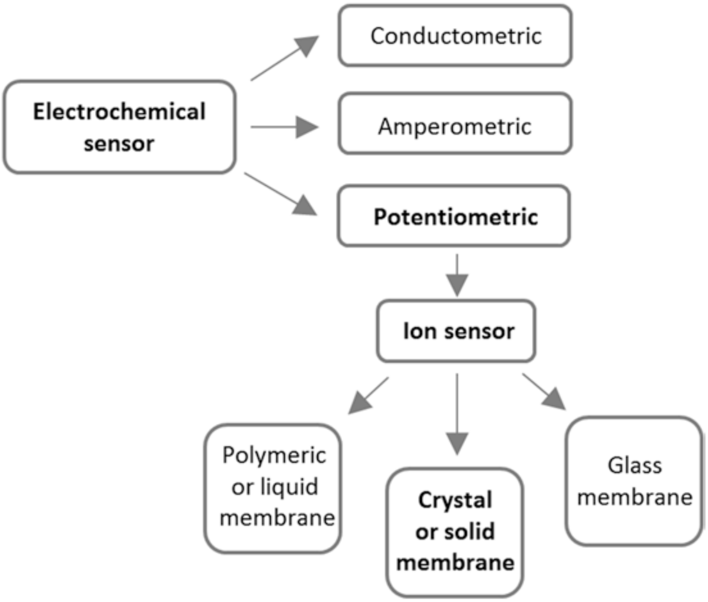

Fig. 16.1 Classification of an electrochemical sensor

potential is constant, and the sensing-electrode potential varies with the concentration of the target ions (Bratovčić et al. 2009). The potential being measured is equal to the difference in potential at the reference electrode and the sensing electrodes.

Key components of AS-ISEs are an ion-selective membrane (ISM) and a transducer or solid contact deposited on a conductive electrode made from carbon, platinum, or gold (Fig. 16.2) (Faridbod et al. 2008; Hu et al. 2016).The role of the ISM is to recognize and select the target ion, while the transducer converts the target-ion concentration to an electrical signal that can be measured against a reference electrode. A silver/silver chloride (Ag/AgCl, Cl^-) electrode is usually used as the reference electrode in ISEs owing to its environmental compatibility, biocompatibility, stable potential, and redox capability (Michalska 2012). A saturated calomel (Hg/Hg_2Cl_2, Cl^-) reference electrode has the advantage of stable potential and is not influenced by light, but is applicable only up to temperatures of about 80 °C. The aforementioned electrodes are currently commercially available; two others, the thallium chloride (Tl (Hg)/TlCl, Cl^-) and the Thalamid™ electrodes are no longer used as reference electrodes owing to toxicity (Guth et al. 2009).

Polymers have been utilized as homogeneous membrane matrices in ISMs owing to good elasticity and mechanical stability (Faridbod et al. 2008). Conductive polymers are often applied as ion-to-electron transducers because of the ohmic properties integrated to a polymer that is flexible and biocompatible (Bobacka et al. 2008). Furthermore, carbon-based materials like carbon nanotubes (CNTs), graphene, and graphene derivatives (e.g., graphene oxide and reduced graphene oxide) have been

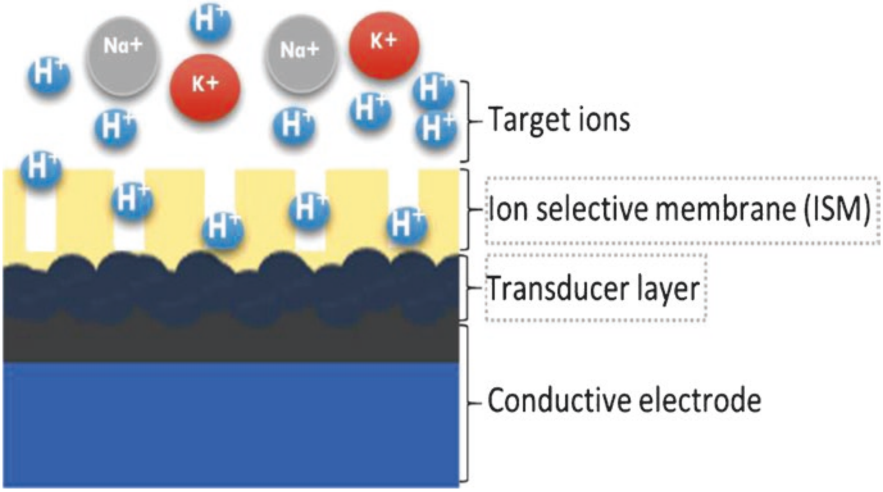

Fig. 16.2 Key components of all-solid-state ion-selective electrodes (AS-ISEs): conductive electrode, solid contact or transducer, and ion-selective membrane

used as transducers in AS-ISEs as their physical, electrical, mechanical, optical, thermal, and chemical properties make them suitable for such use (Yan et al. 2016).

This chapter will introduce readers to the materials in ion-selective membranes and all-solid-state transducers for AS-ISEs. The components of ISMs include a polymeric matrix, ionophores, plasticizers, and ionic additives, while commonly used all-solid-state transducers are conductive polymers of polypyrrole (PPy), polyaniline (PANI), and polythiophene (PT), or carbon-based materials such as carbon nanotubes and graphene.

16.2 Components of an Ion-Selective Membrane

An ion-selective membrane (ISM) cocktail consists of four components: a polymeric matrix, an ionophore as a recognition material, a membrane solvent or plasticizer, and ionic additives. The amount of each component can influence the physical and chemical characteristics of an ISM. Typical composition of an ISM is approximately 33% (w/w) polymeric matrix, 66% (w/w) plasticizer, 1% (w/w) ionophore, and 0.5% (w/w) ionic additives; each component of the ISM depends on the target ion (Faridbod et al. 2008).

16.2.1 Polymeric Matrix Materials

Polymers function as homogeneous membrane matrices for ISMs where their glass transition temperature (Tg) value should be below room temperature (Jadhav et al. 2009). The polymer membrane should be fluid enough under ambient conditions to allow for diffusion of other ISM components. Besides Tg, ISM biocompatibility is especially important for clinical applications; polyvinyl chloride (PVC) is the most commonly used polymer in ISM preparation (Fig. 16.3). Furthermore, acrylate and acrylate derivatives as well as polystyrene have been approved as polymeric matrices for biomedical applications (Faridbod et al. 2008).

16.2.2 Ionophores as Membrane–Active Recognition Components for Ion Carrier and Selectivity

Ionophores provide selectivity towards a target ion owing to their chemical and structural properties. The chemical property involves chemical bond strength and types of molecular interaction, while the structural property includes recognition of size and physical shape of molecular analytes. These specific characteristics influence ISEs selectivity in recognizing the target ions (Ganjali et al. 2006).

Studies have been conducted to understand how the chemical properties of ionophores lead to highly selective ISEs. Wilson et al. (2010) discovered that thioureas – compounds with N-C(S)-N functionality – will significantly improve the selectivity of ISEs towards different metal ions. The presence of intra-molecular interactions, the particular effects by conformational isomerism, and the existence of S and N atoms which act as donor sites make the thiourea derivatives as ligands more versatile (Wilson et al. 2010). Furthermore, the existence of a carbonyl group bonded to the thiourea will result in a heterocyclic compound that provides strong bonding potential as a ligand. The carbonyl group can interact with heavy metal ions such as

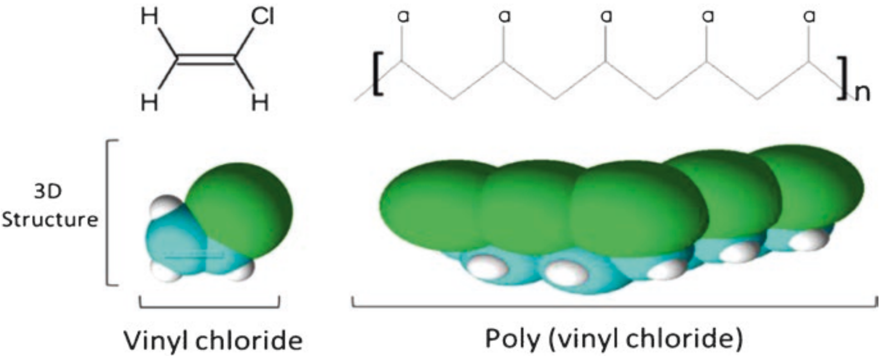

Fig. 16.3 Chemical structure of vinyl chloride and poly (vinyl chloride) (PVC)

Cu(II), Ni(II), and Hg(II) (Saeed et al. 2014). Therefore, thioureas have proved to be attractive ionophores for selective detection of heavy metal ions (Jumal et al. 2012; Ying et al. 2018).

In addition to chemical properties, the structure of an ionophore plays an important role in selectivity towards target ions. The internal cavity of an ionophore whose inner diameter is equivalent to the diameter of the target ions – but not to that of other interfering ions – makes ionophores very selective for ions of interest. In fact, the ionophore is one of the most vital components of the membrane because it is responsible for making the ISEs selective (Pięk et al. 2018).

16.2.3 Plasticizers as Membrane Solvent

A plasticizer is an additive in which the components of the ISM are dissolved; the plasticizer increases the plasticity and fluidity of the material to which it is added. In order to ensure high mobility of the ISM components, a 2:1 weight ratio of plasticizer to polymer is required; the ideal composition of ISMs is 60–66% (w/w) plasticizer and 30–33% polymer matrix. Tables 16.1 and 16.2 summarize the potassium-ion (K^+) and calcium-ion (Ca^{2+}) composition of an ISM, respectively. As can be seen from the tables, both K^+ and Ca^{2+} ISMs have the same components with only a difference in the ionophores. For instance, valinomycin acts as the K^+ ionophore (He et al. 2016; Vanamo and Bobacka 2014; Zhang and Zhang 2013), whereas ETH 129 (Zhao et al. 2019; Park et al. 2017; Ping et al. 2012), and ETH 5234 (ul Haque et al. 2007) act as Ca^{2+} ionophores. The rest of the ISM composition consists of ionic additives, plasticizers, polymer matrix, and solvent. Previous studies have used potassium tetrakis (4-chlorophenyl) borate (KTCPB) (Park et al. 2017; ul Haque et al. 2007; Shiwaku et al. 2018; Guzinski et al. 2017; Vázquez et al. 2002), potassium tetrakis[(3,5-bis[trifluoro methyl]phenyl) borate (KTFPB) (Vanamo and Bobacka 2014; Zhao et al. 2019; Ping et al. 2012), or sodium tetrakis(3,5bis[trifluoromethyl]phenyl) borate (NaTFPB) (Liu et al. 2019) as the ionic additives. The plasticizers are a membrane solvent such as bis(2-ethylhexyl) sebacate (DOS) (He et al. 2016; Guzinski et al. 2017), 2-nitrophenyl octyl ether (2-NPOE) (Ping et al. 2012; ul Haque et al. 2007; Liu et al. 2019), or bis(1-butylpentyl) adipate (BBPA) (Vázquez et al. 2002). Polyvinylchloride (PVC) has been used as the polymer matrix of the membrane (Vanamo and Bobacka 2014; Zhang and Zhang 2013; Liu et al. 2019). Looking into the weight ratio of plasticizer to polymer for K^+-ISMs, Shiwaku et al. used 64.7% DOS plasticizer and 32.7% PVC (Shiwaku et al. 2018), while Vanamo and Bobacka used 62.5% and 33.3% for DOS plasticizer and PVC (Vanamo and Bobacka 2014), respectively. For Ca^{2+}-ISMs, Zhao et al. used 65.6% 2-NPOE plasticizer and 32.8% PVC (Zhao et al. 2019), while Park et al. used 63.5% 2-NPOE plasticizer and 31.7% PVC (Park et al. 2017); both ISM cocktails follow similar ratio of plasticizer to polymer, mainly to ensure high mobility of ISM components.

Table 16.1 Summary of ion-selective membrane composition for K^+

No.	Types of component	Chemical components	Abbreviation	Components amount (% w/w)					
1	Ionophore	Valinomycin		2.0%	1.0%	2.05%	1.0%	1.0%	1.16%
2	Ionic additives	Potassium tetrakis (4-chlorophenyl) borate	KTCPB	0.5%		0.45%			0.32%
3		Potassium tetrakis (3,5-bis [trifluoromethyl] phenyl) borate	KTFPB		0.4%		0.5%	0.2%	
4	Plasticizers	Bis(2-ethylhexyl) sebacate	DOS	64.7%	65. 7%	65.0%	62.5%		
5		2-nitro phenyl octyl ether	2-NPOE					66.0%	
6		Bis (1-butylpentyl) adipate	BBPA						66.4%
8	Polymer matrix	Polyvinylchloride	PVC	32.7%	32.9%	32.5%	33.3%	32.8%	32. 1%
9	Solvent	Tetrahydrofuran	THF	350 μL	1 mL	1.5 mL	-ns-	-ns-	-ns-
References				Shiwaku et al. (2018)	He et al. (2016)	Guzinski et al. (2017)	Vanamo and Bobacka (2014)	Zhang and Zhang (2013)	Vázquez et al. (2002)

ns: not specified.

Table 16.2 Summary of ion-selective membrane composition for Ca^{2+}

No.	Types of component	Chemical components	Abbreviation	Components amount (% w/w)				
1	Ionophore	Calcium ionophore II	ETH 129	1.0%	3.0%		1.0%	0.49%
2		Calcium ionophore IV	ETH 5234			1.0%		
3	Ionic additives	Potassium tetrakis (4-chlorophenyl) borate	KTCPB		1.8%	0.7%		
4		Potassium tetrakis (3,5-bis [trifluoromethyl] phenyl) borate	KTFPB	0.6%			0.2%	
5		Sodium tetrakis(3,5-bis[trifluoromethyl] phenyl)borate	NaTFPB					0.46%
6	Plasticizers	Bis(2-ethylhexyl) sebacate	DOS					
7		2-nitrophenyl octyl ether	2-NPOE	65.6%	63.5%	65.3%	65.8%	66.03%
9	Polymer matrix	Polyvinylchloride	PVC	32.8%	31.7%	33.0%	33.0%	33.02%
10	Solvent	Tetrahydrofuran	THF	1.5 mL		4 mL	-ns-	3.6 mL
11		Cyclohexane			-ns-			
References				Zhao et al. (2019)	Park et al. (2017)	ul Haque et al. (2007)	Ping et al. (2012)	Liu et al. (2019)

ns: not specified.

16.2.4 Ionic Additives as Lipophilic Salts

Ionic additives, also called as lipophilic salts, provide two advantages for the ISMs: increase selectivity towards the target ion and reduce membrane ionic resistance (Morf et al. 2005). With respect to selectivity for divalent cations, a lipophilic anion improves preference for divalent over interfering monovalent cations, and at the same time reduces interference from anionic molecules (Eugster et al. 1991). Therefore, a lipophilic anion will ultimately increase the overall selectivity of ISEs for target divalent cations. Furthermore, the inclusion of ionic additives can act as an ion exchanger, which can improve selectivity when insufficient ionophore is present (Faridbod et al. 2008).

Another advantage of ionic additives is the lowering of ISM ionic resistance, easing the movement of target ions from sample solution into the membrane. Therefore, ionic additives enhance the interfacial ion-exchange kinetics and ultimately reduce the response time of ISEs (Gehrig et al. 1990). Overall, the four components of ISMs complement each other in terms of selectivity, response time, ion-exchange kinetics, fluidity and plasticity of the ISMs. The next section will discuss another important component of an ISE, the transducer.

16.3 Transducer Materials for AS-ISEs

Conductive polymers and nanomaterials as ion-to-electron transducers improve the performance of AS-ISEs in terms of detection limit, sensitivity, selectivity, and chemical stability (Bobacka 2006); these materials enable the miniaturization of ISEs (Hu et al. 2016). Commonly used conductive polymers are polypyrrole (PPy), polyaniline (PANI), and polythiophene (PT) (Fig. 16.4). Commonly used

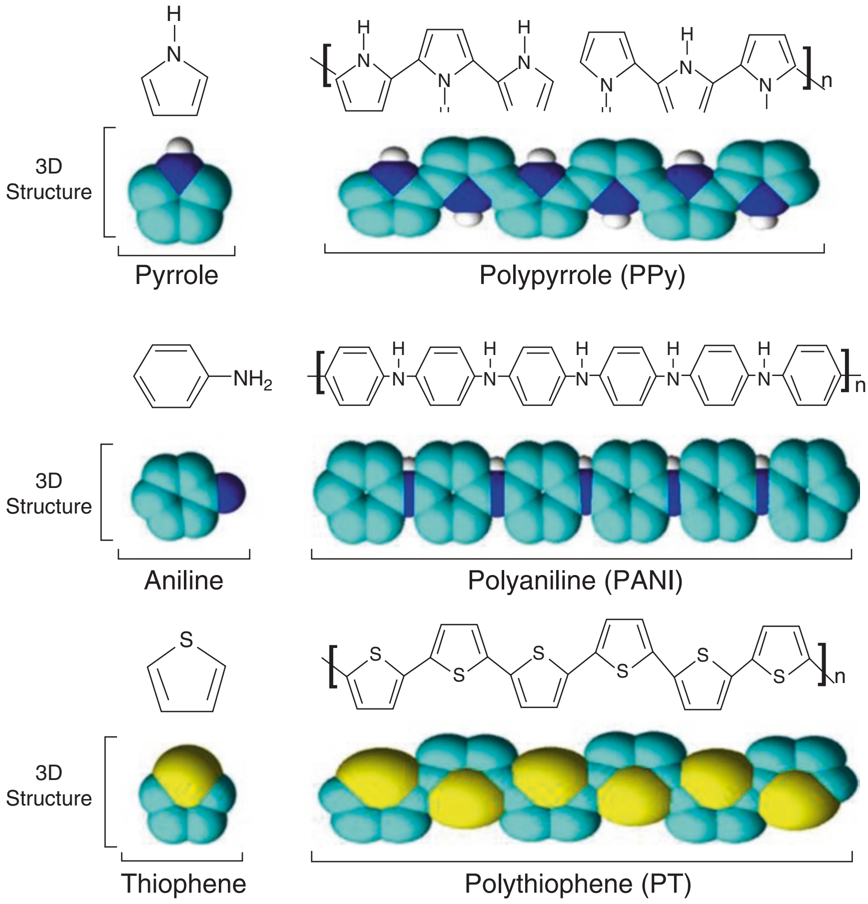

Fig. 16.4 Chemical structure of monomer and polymer units of conducting polymers that have been applied as ion-to-electron transducers in all-solid-state ion-selective electrodes

nanomaterials are three dimensionally–ordered macroporous (3DOM) carbon, colloid-imprinted mesoporous (CIM) carbon, carbon nanotubes (CNTs), graphene, fullerene, nanoclusters and gold nanoparticles (Liu et al. 2019).

16.3.1 Conductive Polymers

Conductive polymers of PPy, PANI, and PT have some key features that make them useful as ion-to-electron transducers (Bobacka 2006; Faridbod et al. 2008; Bobacka et al. 2008). First, conducting polymers can provide ohmic contact with high work function like noble metals and carbon materials. Second, conductive polymers can be deposited from solution onto the conductive electrodes either by electrochemical polymerization or by drop-casting. Third, conductive polymers electroactive property as a result of combinatory effect of electronic and ionic conductivity allows for ion to electron transduction (Faridbod et al. 2008; Bobacka et al. 2008). These are the features that make conducting polymers suitable as solid contact transducers for AS-ISEs.

i. Polypyrrole (PPy)

Polypyrrole has been used as an ion-to-electron transducer in solid-contact ISEs since the beginning of the 1990s and is still used today (Bobacka et al. 2003). PPy as a solid contact enhances the performance of AS-ISEs in terms of Nernstian behavior, linear range, detection limit, and response time (Table 16.3). For example, PPy doped with Titan yellow dye (PPy/TY) as solid contact resulted in a magnesium-selective ISE (Mg^{+2}-ISE); the solid-state electrode has a Nernstian behavior almost equivalent to that of a typical glass electrode (Gupta et al. 2004; Mosayebzadeh et al. 2014). The calibration slope and concentration range for polypyrrole- and non-polypyrrole–based solid contacts were 28.27 ± 0.40 mV per decade within the concentration range of $1.0 \times 10^{-5} – 5.0 \times 10^{-2}$ M, and 29.2 ± 0.4 mV per decade within the concentration range of 9.4×10^{-6} to 1.0×10^{-1} M, respectively (Gupta et al. 2004; Mosayebzadeh et al. 2014). The detection limits of PPy-based and non-PPy-based solid contacts were 6.28×10^{-6} M and 9.4×10^{-6}, respectively, showing not much difference in performance. However, the potentiometric response of PPy-based solid-contact electrodes toward Mg^{+2} was found to be independent of pH from 4.5–8.0, while non–PPy–based solid contacts were independent of pH from 3.5–7.8 (Gupta et al. 2004; Mosayebzadeh et al. 2014). Polypyrrole-based Mg^{+2}-ISEs showed fast response time compare to non-PPy-based Mg^{+2}-ISEs, < 10 s and 13 s, respectively (Mosayebzadeh et al. 2014). The results show that a PPy solid contact is comparable to a non-solid state one.

ii. Polyaniline (PANI)

Polyaniline (PANI) is utilized in ISEs fabrication owing to its stable potential, easy preparation, and low cost (Shishkanova et al. 2005). PANI has been used as a solid contact (Jiang et al. 2019), or as a component of an ion-selective membrane

Table 16.3 Linear range, detection limit, and response time of polypyrrole as solid contact in AS-ISEs

Transducer	Target ion	Application	Linear range	Detection limit	Response time	Reference
GCE/PPy-rGO	Nitrate ion (NO_3^-)	Agricultural	10^{-5} to 10^{-1} M	$10^{-5.2 \pm 0.1}$ M	≤15 s	Pan et al. (2016)
CSPE/PPy	Iron ion (Fe^{2+})	Biological, industrial, environmental	1×10^{-6} to 1×01^{-1} M	8.78×10^{-7} M	–	(Gholami et al. (2015)
PGE/PPy-TY	Magnesium ion (Mg^{2+})	Medical	1.0×10^{-5} to5.0×10^{-2} M	6.28×10^{-6} M	<10 s	(Mosayebzadeh et al. (2014)
PGE/PPy	Arsenate ion (AsO^{3-})	Environmental	5.0×10^{-5} to 1.0×10^{-1} M	2.8×10^{-5} M	≤10 s	(Ansari et al. (2013)
PGE/PPy	Uranyl ion (UO^{2+})	Environmental	1.0×10^{-6} to 1.0×10^{-2} M	6.30×10^{-7} M	≤12 s	(Ansari and Mosayebzadeh (2013)
PGE/PPy	Zinc ion (Zn^{2+})	Environmental	1.0×10^{-5} to 1.0×10^{-1} M	8.0×10^{-6} M	–	(Ansari et al. (2012)

PGE: Pencil graphite electrode
rGO: Reduce graphene oxide
TY: Titanium yellow
PPy: Polypyrrole
GCE: Glass carbon electrode
CSPE: Screen-printed carbon electrode

(Aytaç et al. 2004). In addition, PANI can exist as either film, microfiber, or nanoparticle; PANI in microfiber form enhances ISE performance owing to its hydrophobicity, which minimizes water intake into the ISM (Jiang et al. 2019). As an example, electrospun PANI-polystyrene microfiber film (e-PANI-PS) was used as a transducer in solid-contact ISEs to sense lead ion (Pb^{2+}). The Pb^{2+}-ISEs based on e-PANI-PS exhibited a wide linear detection range (10^{-8} to 10^{-3} mol/L), a low detection limit (~5×10^{-9} mol/ L), a Nernstian slope of 29.1 mV/decade, and a fast response time (< 10 s) (Jiang et al., 2019). Moreover, the fabricated ISEs demonstrated a lower detection limit for Pb^{2+} and better potential stability compared to ISEs fabricated using drop-cast PANI-PS films. The analytical performance of the e-PANI-PS microfiber transducer for Pb^{2+} detection is a result of the high hydrophobicity that minimizes water uptake. Furthermore, e-PANI-PS has higher capacitance and lower impedance than the drop-cast PANI-PS, which promoted fast ion-to-electron transfer at the electrode-solution interface (Jiang et al. 2019). These features make PANI one of the most used conductive polymers as a transducer for AS-ISE fabrication.

iii. Polythiophene (PT)

The first polythiophene used as a solid contact in ISEs was poly(3-octylthiophene) (POT) (Bobacka et al. 2008). Poly(3,4-ethylene-dioxythiophene) (PEDOT) in its p-doped form is highly electroactive and possesses good environmental stability (less sensitive to O_2 and CO_2) compared to transducers based on PPy as solid contact (Bobacka 2006). Therefore, water-dispersible PEDOT with poly(styrenesulfonate) (PEDOT:PSS) (Fig. 16.5) was used as an ion-to-electron transducer in solid-contact ISEs for detection of certain ions: potassium (K^+), silver (Ag^+), sodium (Na^+), cesium (Cs^+), calcium (Ca^{2+}), and some aromatic cations (e.g., N-methylpyridinium, bupivacaine) (Bobacka et al. 2008). However, few research

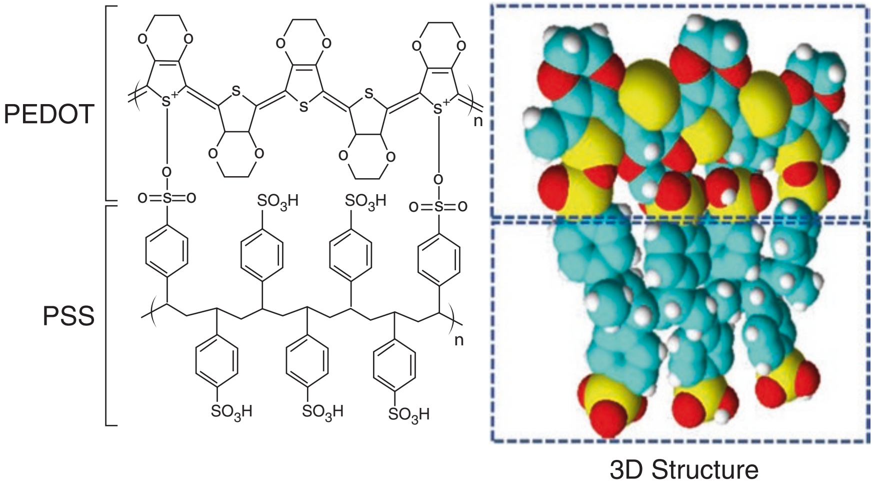

Fig. 16.5 Chemical structure of poly (3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS)

reports on PEDOT:PSS use as an electrochemical sensor owing to poor adhesion of PEDOT:PSS on conductive electrode surfaces. In aqueous solution, PSS can result in swelling of PEDOT:PSS and the film can be removed from the electrode surface (Wang et al. 2014; Benoudjit et al. 2018), limiting PEDOT:PSS use as a transducer for AS-ISEs. Therefore, some studies focus on enhancing the adhesion of PEDOT:PSS on electrode surface by using polyvinyl alcohol (PVA) (Wang et al. 2014) and sodium carboxymethyl cellulose (Na-CMC) (Zhang et al. 2015) binders, or depositing PEDOT:PSS with electro-polymerization instead of by drop-casting (Benoudjit et al. 2018). The resulting improvement allows PEDOT:PSS to be an effective transducer for AS-ISEs.

16.3.2 Nanomaterials

Recently, nanomaterials have been suggested as transducer materials for AS-ISEs (Liu et al. 2019). Three-dimensionally ordered macroporous (3DOM) carbon (Lai et al. 2007), colloid-imprinted mesoporous (CIM) carbon (Hu et al. 2014), carbon nanotubes (CNTs) (Ganjali et al. 2010; Crespo et al. 2008), graphene (Ping et al. 2011), fullerene (Fouskaki and Chaniotakis 2008), nanoclusters (Zhou et al. 2012), and gold nanoparticles (Jaworska et al. 2011) are commonly used nanomaterials as a result of their high surface area, intrinsic hydrophobicity, and electric conductivity. Furthermore, these nanomaterial-based ISEs exhibit high potential stability and have shown more excellent resistance to O_2, CO_2, light, and redox interferences than do the classical conducting polymers (Liu et al. 2019). These features make these nanomaterials suitable as transducer materials for AS-ISE fabrication. Generally, nanomaterial-based solid contacts are prepared layer by layer using drop-casting methods. However, it should be noted that nanomaterials can easily detach from an electrode surface owing to poor adhesion (Liu et al. 2019). Although PVC has been successfully used as a facile and effective binder to fabricate nanomaterial-based solid contact (Hu et al. 2014), the electrical conductivity of nanomaterials might be reduced by the poor conductivity of PVC.

More recently, we utilized PEDOT:PSS with reduced graphene oxide (rGO) nanomaterial as solid contact for biosensors because the composite showed good adhesion to the electrode surface while retaining good conductivity (Ismail et al. 2019). From electrochemical analyses by cyclic voltammetry (CV), the transducer showed a high effective surface area of 0.219 mm^2 and a high peak current of 0.793 mA. The high conductivity is further confirmed with electrical impedance spectroscopy (EIS), showing the composite to have low charge-transfer resistance (R_{ct}) of 200.7 Ω (Ismail et al. 2019). The CV and EIS results suggest that rGO-PEDOT:PSS composite has the potential to be used as solid contacts for AS-ISEs.

16.4 Summary

This chapter introduces the materials used for fabricating the components of AS-ISEs: the ion-selective membrane (ISM) and the all-solid-state transducer. The role of an ISM is to recognize and select the target io; the ISM consists of four components: polymeric matrix, plasticizer, ionophore, and ionic additives. The physical and chemical characteristics of AS-ISEs can be influenced by the amount of each component, and the typical cocktail mix for an ISM is polymeric matrix 33% (w/w), plasticizer 66% (w/w), and ionophore 1% (w/w). Polyvinyl chloride (PVC) functions as a homogeneous membrane matrix for the other ISM components. Ionophores provide selectivity towards a target ion, which is also known as membrane-active recognition; selection of ionophore depends on the target ion. Plasticizers are responsible for controlling the physical property (plasticity or fluidity) of ISMs. Ionic additives are ion exchangers that ensure the permselectivity of the ISMs if no or insufficient ionophore is present. The solid-state transducer converts the target-ion concentration to an electrical signal that can be measured. Materials used as solid-state transducers are conductive polymers and nanomaterials. Common conductive polymers used in AS-ISEs are polypyrrole, polythiophene, and polyaniline, owing to their intrinsic characteristics. Nanomaterials such as Three-dimensionally-ordered macroporous carbon, colloid-imprinted mesoporous carbon, carbon nanotubes, graphene, fullerene, nanoclusters, and gold nanoparticles are good solid contacts for AS-ISEs owing to their ion-to-electron transduction. Reduced graphene oxide can be combined with PEDOT:PSS to serve as a solid contact for AS-ISEs.

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