J Solid State Electrochem (2012) 16:3253–3260
DOI 10.1007/s10008-012-1768-6

ORIGINAL PAPER

A pH-controllable electrochemical molecule switch employing a new electrochemical measurement system as switching transducer

Wei Gao · Naiying Wu · Junfeng Song

Received: 16 April 2012 / Revised: 28 April 2012 / Accepted: 30 April 2012 / Published online: 15 May 2012

Abstract A new design concept of electrochemical pH-controllable molecular switch is presented by utilizing a new electrochemical measurement system as switching transducer. A pH sensor is connected in series between the terminal points of the working and counters electrodes of a potentisostat, and immersed in the solution together with a reference electrode, establishing a novel electrochemical measurement system. In this system, the variation of pH-controllable interface potential at the pH-sensing film/solution interface can be converted to current response when amperometry technique is employed. Based on this unique current–potential relationship, a pH-controllable switch is designed to monitor the protonation and deprotonation reaction of pH-sensing molecule. The current direction interchanges between positive and negative via pH control, illustrating a reversible conformation transition between protonated state and deprotionated state of molecule. The magnitude of current value represents the degree of protonation and deprotonation reaction of molecule. The strategy is successfully demonstrated with a remarkably reversible polyaniline-based pH-controllable switch, which confirms the feasibility of the novel electrochemical measurement system as switching transducer for designing electrochemical pH-controllable switches. This study may open up a potential avenue to construct the electrochemical pH-controllable switches.

Keywords pH switch · Electrochemical measurement system · Amperometry · Zero current potentiometry · $E_{zcp}(pK_a)$

Introduction

Development of molecular switches is of considerable practical and fundamental significance to the fields of drug delivery systems and sensor device fabrications [1]. As a representative, the pH-controllable switches have been an area of intense research activity. In principle, a reliable pH-controllable molecular switch generally meets three conditions. Firstly, pH change in aqueous solutions can induce an interchangeable molecular system involving at least two distinct states, such as protonation and deprotonation [2], assembly and disassembly of polymers [3], or molecular recognition of molecule held through hydrogen bonding [4]. Secondly, there is a distinct variation of a specific physical or chemical property between these two states of molecular system. Finally, it is particularly necessary that an appropriate device can be chosen as the switching transducer to monitor the variation of the properties and efficiently convert it to an 'on/off' signal.

By utilizing this criterion, various pH-controllable switches have been designed. Good examples are the multitudinous photochemical switches where two stable states of the pH-

W. Gao · J. Song
Department of Chemistry, Fudan University,
Shanghai 200433, China

W. Gao (✉)
Institute of Analytical Science, Northwest University,
Xi'an 710069, China
e-mail: gaowei2003425@163.com

N. Wu
Department of Chemistry, Shangqiu Normal University,
Shangqiu 476000, China

Present Address:
W. Gao
Hebei Engineering Technology Research Center of Natural Pigments,
Handan 057250, China

controlled molecular switching system are distinguished by different photochemical properties, which can be easily monitored by different photochemical analytical instruments and converted into an 'on/off' responses of fluorescence [5–7], luminescence [8–10], UV–vis absorbance [11–13], CD spectrum [14, 15], photocurrent [16] or ^{1}H NMR spectrum [17–19]. In contrast, there is a paucity of study on the electrochemical pH-controllable switches. According to aforementioned three necessary conditions of a pH-controllable switch, one important reason for this situation may be the lack of suitable electrochemical devices or techniques as the switching transducer. The desirable molecular switching systems are generally based on the acid–base dissociation equilibrium of a molecule, or the gain and lost of the hydrogen bonding between two molecules in order to ensure the high reversibility. Thus, a successful pH switch must involve at least one process of the protonation and deprontonation of molecule. Such a process may lead to more change of electrostatic properties of molecule than redox properties from the electrochemical point of view. However, it is pity that most currently universal electrochemical techniques such as various voltammetric methods are suitable for studying the redox property of molecule [20], but fail in investigating the electrostatic property of molecule. Despite a few techniques such as electro-osmotic mobility measurements [21, 22] and molecular probe measurements [23, 24] can do this, they are so professional that they are rarely seen in most of labs. Therefore, the prospective of the use of conventional electrochemical devices or techniques to design electrochemical switching is very limited.

Recently, we have reported a new electrochemical measurement system for investigating the surface acid–base dissociation property of the solid-state pH sensors [25, 26]. In this system, a pH sensor is connected in series between the terminal points of the working and counter electrodes of a potentisostat, and immersed in the solution together with a reference electrode. When an external potential is applied on the sensor against the reference electrode, the resulting current response depends on not only the external applied potential but also the interface potential at the pH-sensing film/solution interface. When the applied potential is fixed, the current is entirely determined by the interface potential. Since the interface potential is a function of the solution pH, we can use the solution pH as a controllable parameter to modulate the current value and direction. This opens the possibility to design the amperometric pH sensor or amperometric pH-controllable switches. The strategy of designing amperometic pH sensor has been successfully demonstrated on the example of an amperometric pH sensor based on polyaniline (PANI) film [25].

In this study, we will disclose the strategy of developing the amperometric pH-controllable switch based on utilizing the proposed new measurement system as switching transducer. The fundamental principle is discussed, and the previously established polyaniline (PANI)-based amperometric pH sensor [25] is employed to demonstrate the common construction program of an amperometric pH-controllable molecule switch. This study may open up an entirely new avenue for designing the electrochemical pH-controllable switches.

Experimental

Materials and apparatus

Aniline and other reagents were obtained from Shanghai Chemical Reagent Ltd., China. A series of Britton–Robinson (B–R) buffers of pH 1.81–9.91 were prepared for pH measurements. All chemicals were of analytical reagent grade. Twice distilled water was used throughout. The pencil leads (type PL-920 and PL-912, black lead of degree 2B) were purchased from a local Lotus store in China. All leads had a total length of 30 mm and a diameter of 0.5 mm.

The pH of the buffers was measured using a pH meter (Hanna, pH-211, Italy). All electrochemical experiments were performed using a CHI 660 electrochemical workstation (CH Instruments, USA).

Preparation of PANI film-based pH sensor

The body of the PANI film-based pH sensor was a pencil lead (Fig. 1a). Two ends of the pencil lead were entwined by the copper wires (diameter 0.2 mm) to establish the electrical contact. The bonding pad and the copper wire were covered with the insulating adhesive plaster.

PANI film was synthesized electrochemically on the surface of self-made pencil graphite electrode from 1 M H_2SO_4 solution containing 0.1 M aniline by using cyclic voltammetry in a conventional three-electrode system, in which the self-made pencil graphite electrode acted as working electrode, a platinum wire acted as counter electrode and a saturated calomel electrode (SCE) acted as the reference electrode. The potential was scanned between −0.1 and 1.2 V for the first cycle and between −0.1 V and 0.85 V at a scan rate of 50 mV s^{-1} for the following 20 cycles. The resulting PANI film-based pH sensor was rinsed with water and kept in air for 6 h.

Establishment of PANI-based amperometric pH-controllable switch

As shown in Fig. 1b, a PANI-based pH sensor was connected in series between the terminal joints of the working and counter electrode of a potentiostat. The sensor and a SCE were immersed into the solution, establishing a new measurement system. A 10-ml volume of the B–R buffer of a selected pH in the range of 1.81–9.91 was introduced into a culture

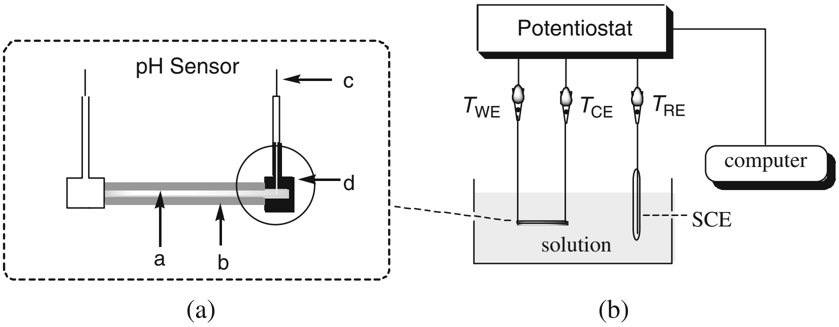


Fig. 1 **a** Schematic diagram of the PANI film-based pH sensor. **a** Pencil lead, **b** PNAI film, **c** copper wire, **d** insulating adhesive plaster. **b** Schematic illustration of the new electrochemical measurement system. T_{WE}, T_{CE}, and T_{RE} are the terminal joints of working electrode, counter electrode, and reference electrode of a potentiostat, respectively. *SCE* indicates the saturated calomel reference electrode

dish (diameter 5.5 cm). With the new system, linear sweep voltammmetry was carried out from −0.6 to 1.0 V at a scan rate of 100 mV s^{-1} to determine the initialized potential of amperometric switch. The PANI-based amperometric pH-controllable switch was obtained by setting the initialized potential at 0.088 V in amperometric measurement.

Theory

Figure 1 schematically depicts the establishment of a novel electrochemical measurement system. A solid-state pH sensor is connected in series between the terminal joints of the working electrode (T_{WE}) and counter electrode (T_{CE}) of a potentiostat, and then immersed into the aqueous solution together with a reference electrode.

Figure 2a, b briefly shows the electronic circuit diagram and analog electronic circuit of the new measurement system, respectively. The system consists of two circuits: a potential circuit and a current circuit. In current circuit, the current I flows through the terminal joint T_{CE} of the counter electrode, pH sensor S and the terminal joint T_{WE} of working electrode, to the virtual earth. Obviously, the distinct connection excludes the possibility of the current flowing through the sensor/solution interface and the electrolyte solution. The current should be a direct current that abides by Ohm law, and its value rests with the resistance R_w of the current circuit and the working voltage U_W of the current circuit.

$$I = U_W/R_W = U_W/(R_s + R_o) \tag{1}$$

where I is the circuit current, R_w is the whole resistance of current circuit mainly containing the resistance R_s of pH sensor and other resistances R_o of current circuit.

The potential circuit is used to apply the working voltage to drive the current. As shown in Fig. 2, assumed that no external potential E is applied, the sensor, the reference electrode, and the solution actually build a galvanic cell. In this case, the electromotive force of the cell will be responsible for the working voltage U_W.

$$U_W = E_{cell} = \varphi - E_{ref} \tag{2}$$

where E_{cell} is the electromotive force of the cell, φ is the potential of the pH-sensing film/solution interface, and E_{ref} is the potential of the reference electrode.

However, when an external potential is applied, it also makes a contribution to the working voltage U_W. Because its direction is opposite in sign to the existing electromotive force, the working voltage U_W becomes

$$U_W = E_{cell} - E = (\varphi - E_{ref}) - E \tag{3}$$

where E is the external applied potential.

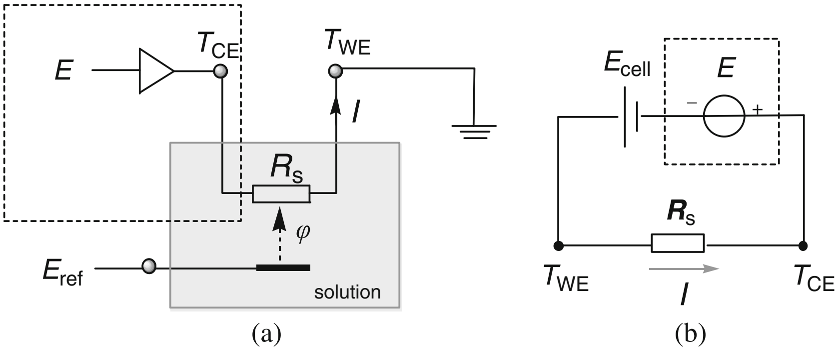


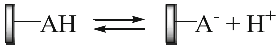
Fig. 2 **a** Electronic circuit diagram. E, E_{ref}, and φ indicate the external applied potential, reference potential of the reference electrode, and interface potential of the PANI film/solution interface, respectively, I is the circuit current. **b** Scheme of analog electronic circuit. R_s is the resistance of pH sensor. E_{cell} is the electromotive force of the cell

With the drive of the working voltage U_W, a direct current generates in current circuit.

$$I = [(\varphi - E_{\mathrm{ref}}) - E)]/(R_s + R_o) \tag{4}$$

Equation (4) describes the fundamental current–potential characteristics of the new electrochemical measurement system. Here, the reference potential E_{ref} and the current resistance (R_s+R_o) usually keep constant as the same reference electrode and pH sensor are used. Hence, the current are substantially codetermined by two variable parameters: the interface potential φ and the applied potential E. The interface potential φ is a hidden chemical variable that is a function of the solution pH due to the pH-sensitive property of the sensing film. The applied potential E is a controllable instrumental parameter, which value rests with the used controlled-potential technique. Therefore, the current can be modulated by simultaneously changing the solution pH and initializing different applied potential. Once amperometry has been employed in the new measurement system and the applied potential E has been also initialized as a constant, the current should be entirely controlled by the solution pH, which offers a possibility for designing the pH-controllable switch.

Let AH be a molecule group of the pH-sensing film, the acid–base equilibrium reaction occurring at the interface of pH-sensing film/solution may be written as:



The corresponding expression of the solution pH is

$$\mathrm{pH} = \mathrm{p}K_a + \log[\mathrm{A}^-]/[\mathrm{AH}] \tag{5}$$

where [] represent the concentration.

According to literatures [27], the interface potential φ can be expressed as:

$$\varphi = -2.303(\alpha RT/F)\mathrm{pH} + C_1 \tag{6}$$

where α is the pH sensitivity factor, R is the universal gas constant, T is the temperature (K), and F is the Faraday constant, C_1 is a constant value related to chemical property of the pH-sensing material.

Substitution of Eqs. (5) in (6) leads to an expression for the relationship between interface potential and conformation transition of molecule.

$$\begin{aligned}\varphi = &-2.303(\alpha RT/F)\mathrm{p}K_a \\ &- 2.303(\alpha RT/F)\log[\mathrm{A}^-]/[\mathrm{AH}] + C_1\end{aligned} \tag{7}$$

In Eq. (7), the pK_a value is a good indicator for molecule conformation, at which the [AH] is just equal to the [A$^-$]. Thus, when the solution pH is at pK_a, the interface potential φ is

$$\varphi(\mathrm{p}K_a) = -2.303(\alpha RT/F)\mathrm{p}K_a + C1 \tag{8}$$

With the substitution of φ(pK_a), Eq. (7) is simplified to

$$\varphi = \varphi(\mathrm{p}K_a) - 2.303(\alpha RT/F)\log[\mathrm{A}^-]/[\mathrm{AH}] \tag{9}$$

The pK_a value is a constant value as to a given material, and thus the interface potential φ(pK_a) also should have a constant value. Accordingly, the φ(pK_a) value can also be viewed as a good indicator to distinguish the conformation of molecule. At pH lower than pK_a, the [AH] is higher than the [A$^-$] and the interface potential φ is larger than the φ(pK_a). At pH higher than pK_a, the [AH] is lower than the [A$^-$] and the interface potential φ is smaller than the φ(pK_a).

Combination Eqs. (4) and (9) yields:

$$I = \langle\{\varphi(\mathrm{p}K_a) - 2.303(\alpha RT/F)\log[\mathrm{A}^-]/[\mathrm{AH}] - E_{\mathrm{ref}}\} - E\rangle/(R_s + R_o) \tag{10}$$

As expressed by Eq. (10), the current is closely related to the conformation transition between protonated state AH and deprotonated state A$^-$, and its value and direction are determined by the difference between the term $\{\varphi(\mathrm{p}K_a) - 2.303(\alpha RT/F)\log[\mathrm{A}^-]/[\mathrm{AH}] - E_{\mathrm{ref}}\}$ and the term E. According to Eq. (10), if pH of the solution is at pK_a and simultaneously the initialized applied potential E_i is equal to the term$\{\varphi(\mathrm{p}K_a) - E_{\mathrm{ref}}\}$, the current I should be zero. In this case, when amperometric measurement is performed, a pH-controllable switch of the current should be established. At lower pH than pK_a, the direction of current I is positive because AH dominates and the term$\{\varphi(\mathrm{p}K_a) - 2.303(\alpha RT/F)\log[\mathrm{A}^-]/[\mathrm{AH}] - E_{\mathrm{ref}}\}$ is higher than the term E_i (i.e., $\{\varphi(\mathrm{p}K_a) - E_{\mathrm{ref}}\}$). At higher pH than p$K_a$, the direction of current I is negative because A$^-$ dominates and the term$\{\varphi(\mathrm{p}K_a) - 2.303(\alpha RT/F)\log[\mathrm{A}^-]/[\mathrm{AH}] - E_{\mathrm{ref}}\}$ is lower than the term E_i (i.e., $\{\varphi(\mathrm{p}K_a) - E_{\mathrm{ref}}\}$). The reversible alternation of the current direction between positive and negative controlled by the pH change just reflects the conformation transition of the protonated and depronated states of molecule. The magnitude of current value represents the degree of protonation and deprotonation reaction of molecule. The higher the current value is, the greater the protonated degree of molecule becomes. In reverse, the lower the current value is, the greater the deprotonated degree of molecule becomes.

Results and discussion

Because of the famous pH-sensitive property of PANI [28–30], the PANI film-based amperometric pH sensor established previously by us is taken as the example to demonstrate the theory. As shown in Fig. 3, the key

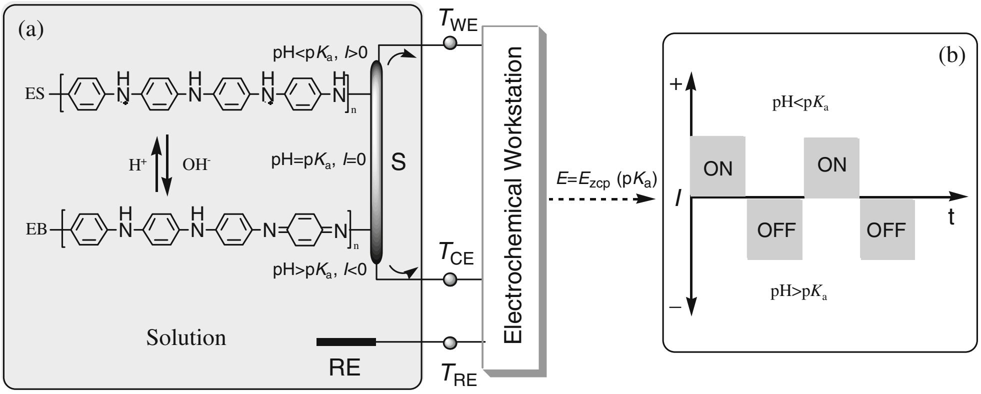


Fig. 3 Schematic illustration for the PANI film-based pH-controllable switch

molecular switching system is the protonation and deprotonation reaction of PANI film coated on a pencil graphite electrode reported by our recent study [25]. The emeraldine salt (ES)–emeraldine base (EB) transition modulated via pH control arouses a reversible interface potential variation at the interface of PANI film and solution, which is monitored by the new measurement system acting as the switching transducer and converted to an 'on/off' signal of current direction between positive and negative. Details about the process of establishing this switch is described as follows.

Selection of the initialized applied potential

As mentioned in "Theory" section, the first task is the selection of the initialized applied potential E_i in amperometric measurement. Herein, we propose zero current potentiometry [26] for determining the desirable initialized applied potential E_i. With the new electrochemical system, linear sweep voltammetry was carried out from −0.6 to 1.0 V in a serious of Britton–Robinson buffers of pH 1.81–9.91. As shown in Fig. 4 (also presented as Fig. 2 in literature [25]), at a given pH value, the voltammogram exhibited a good linearity, illustrating the unique current–potential characteristics of the new measurement system expressed in Eq. (4). The slope^{-1} of the linear voltammogram denoted the whole resistance R_w in current circuit of the new system. Upon the increase of the pH, the linear voltammograms shifted negatively in parallel along the potential axis. Obviously, such a parallel shift indicated that almost no change occurred in the whole resistance in current circuit. Hence, although the resistance of PANI film has proved to vary with the pH of solution [31–33], the variation can be neglected because the resistance of PANI film is too less than that of the pencil lead. The resistance of pH sensor can be viewed as a constant value independent of the pH values.

The pH-dependent shift of the linear voltammogram also reflects the excellent pH-sensitive property of PANI film. We can measure the potential shift at the same current level to investigate the pH-sensitive property of PANI. As shown in Fig. 4, the applied potential when the current is zero is more easily detected than other detectable potentials. Define

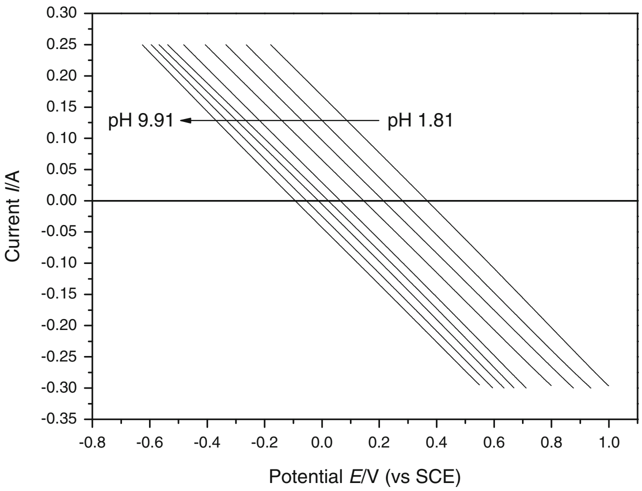


Fig. 4 Linear sweep voltammograms of the PANI film-based pH sensor in the B–R buffers of pH 1.81–9.91

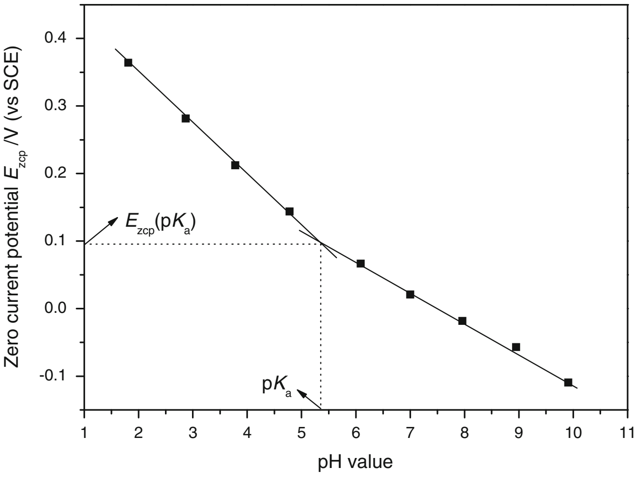


Fig. 5 Plot of zero current potential E_zcp as a function of pH

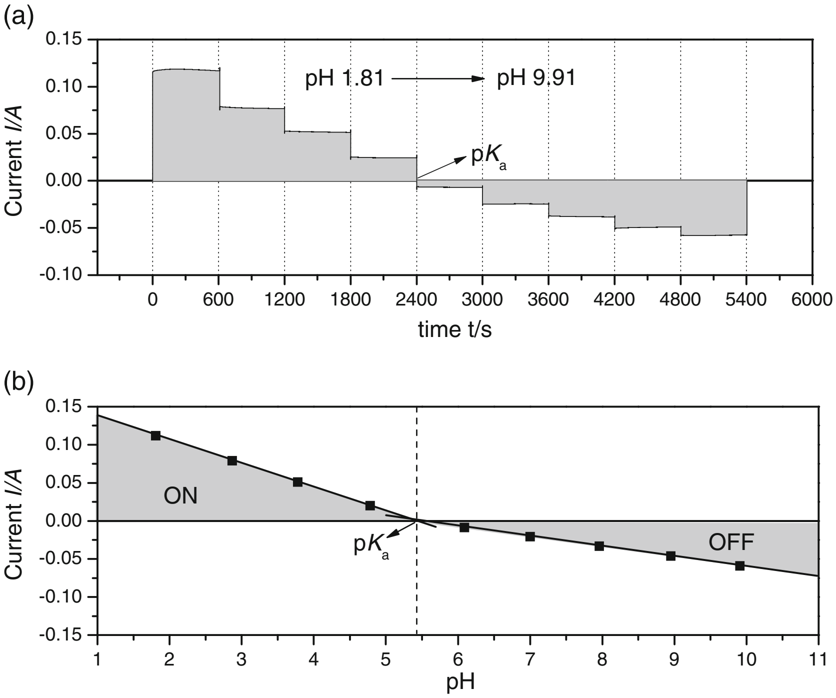


Fig. 6 **a** Amperometric *I–t* curve at the inilialized potential E_i of 0.088 V, **b** plot of the current versus the pH

the applied potential as zero current potential E_{zcp}, its expression is deduced from Eq. (4)

$$E_{zcp} = \varphi - E_{ref} \tag{11}$$

Equation (11) indicates that when the applied potential E is equal to E_{zcp}, the external applied potential E just compensates the electromotive force E_{cell} of the cell spontaneously existing in the new electrochemical system, and thus no current generates in the system. Apparently, because the influence of the resistances in current circuit is eliminated in Eq. (11), zero current potential E_{zcp} should be more accurate than other detectable potentials. The technique of measuring zero current potential E_{zcp} is named as zero current potentiometry.

The plot of zero current potential E_{zcp} against the pH is presented in Fig. 5. Two good linear regions were observed according to the following equations: E_{zcp}=0.4964–0.0743pH (pH 1.81–5.43) and E_{zcp}=0.3394–0.0448pH (pH 5.43–9.91). The intersection point at pH 5.43 compares favorable with the surface pK_a of emeraldine form ranging from 5 to 8 reported in literature [28–30], indicating that PANI film in this study mainly exists in the form of the emeraldine. The occurrence of different slopes in two pH regions is ascribed to the pH-dependent ES–EB transition of PANI film (Fig. 3). In the region of pH 1.81–5.43, both of two imine groups of EB participate in protonation while only one imine group is protonated in the pH range of 5.43–9.91. Therefore, the slope (44.8 mV/pH) of the plot of the E_{zcp} versus pH in the high pH region is almost half of that (74.3 mV/pH) in the low pH region.

Introducing the pK_a value into the above two linear equations, zero current potential E_{zcp}(pK_a) (i.e., $\{\varphi\ (\mathrm{p}K_a) - E_{ref}\}$) with pH=p$K_a$ was calculated to be 0.088 V. As shown in Fig. 5, when the applied potential E was equal to E_{zcp}(pK_a) and the pH of solution was at pK_a, the current was zero. This meets the requirement of the initialized applied potential E_i in proposed switch. Therefore, the initialized applied potential E_i in designing the PANI film-based pH-controllable switch is selected as 0.088 V.

pH-controlled switching response

Initializing the applied potential at 0.088 V, the amperometric measurement was carried out across a pH gradient ranging from pH 1.81 to 9.91. The amperometric curve (Fig. 6a)

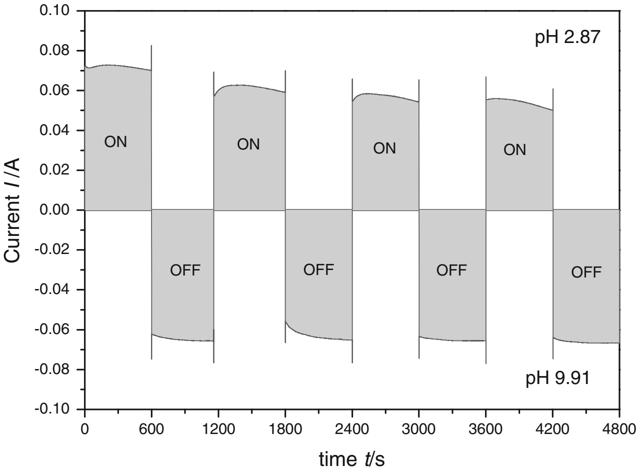


Fig. 7 pH-controlled switching response of the current direction

showed that the current decreased with the increase of the solution pH. Plotting the current versus the pH (Fig. 6b), it was found that two good linear regions intersected at 5.54, which was in agreement with the pK_a measured by zero current amperometry. As seen from Fig. 6b, when the solution pH was at pK_a, the current was just zero; when pH is lower than 5.54, the current direction was positive; when pH was higher than 5.54, the current direction was negative. The magnitude of current value reflected the degree of protonation and deprotonation reaction of PANI. The higher the current value was, the more the ES occupied on the surface of PANI film. In reverse, the lower the current value was, the more the EB state occupied on the surface.

The amperometric measurement was performed by repeatedly changing the pH between 2.87 and 9.91, a typical pH-controllable switching response was obtained. As shown in Fig. 7, The PANI-based sensor generated a positive current at pH 2.87, while it generated a negative current at pH 9.91. This switching behavior in the current direction showed good reversibility. All the evidences confirm our design concept of the electrochemical pH switch where the current can be switched between positive and negative by changing the pH of the solution, illustrating the pH-dependent ES–EB transition of PANI.

Conclusions

A novel design concept for pH-controllable molecule switch has been developed based on using a new electrochemical measurement system as switching transducer. Equations for describing the design concept of pH-controllable molecule switch are derived. In the switch, the reversible alternation of the current direction between positive and negative controlled by the pH change reflects the conformation transition of the protonated and depronated states of molecule. The magnitude of current value represents the degree of protonation and deprotonation reaction of molecule. A PANI-based pH-controlled switching of current is successfully established to demonstrate the design concept.

Considering high popularization of the potentiostat in the researches all over the world, this study might provide a promising way in the development of the pH-controllable switches. A range of super-molecules or bio-macromolecules containing the pH-sensitive groups such as carboxylic groups, hydroxyl groups, and amine groups generally undergo the protonation and deprotonation reactions in different pH values. These reactions can be envisioned to design various electrochemical pH-controllable switches utilizing the proposed measurement system.

Acknowledgments The present work was supported by the National Natural Science Foundation of People's Republic of China (grant no. 20475043).

References

1. Feringa BL (2001) Molecular switches. Wiley-VCH, Weinheim
2. Gao F, Chen X, Zhou F, Weng LP, Guo LT, Chen M, Chao H, Nian L (2009) pH responsive luminescent switches of ruthenium(II) complexes containing two imidazole groups: synthesis, spectroscopy, electrochemistry and theoretical calculations. Inorg Chim Acta 362:4960–4966
3. Dalmau M, Lim S, Wang SW (2009) Design of a pH-dependent molecular switch in a caged protein platform. Nano Lett 9:160–166
4. Chakrabarti S, Mukhopadhyay P, Lin S, Isaacs L (2007) Reconfigurable four-component molecular switch based on pH-controlled guest swapping. Org Lett 9:2349–2352
5. Shiraishi Y, Tokitoh Y, Nishimura G, Hirai T (2005) A molecular switch with pH-controlled absolutely switchable dual-mode fluorescence. Org Lett 7:2611–2614
6. Liu H, Zhou Y, Yang Y, Wang W, Qu L, Chen C, Liu D, Zhang D, Zhu D (2008) Photo-pH dually modulated fluorescence switch based on DNA spatial nanodevice. J Phys Chem B 112:6893–6896
7. Zhu X, DeGraaf J, Winnik FM, Leckband D (2004) Tuning the interfacial properties of grafted chains with a pH switch. Langmuir 20:1459–1465
8. McCoy CP (2006) Soft matter pH sensing: from luminescent lanthanide pH switches in solution to sensing in hydrogels. Chem Mater 18:4336–4343
9. Chen YM, Liu YJ, Li Q, Wang KZ (2009) pH- and DNA-induced dual molecular light switches based on a novel ruthenium(II) complex. J Inorg Biochem 103:1395–1404
10. Han MJ, Gao LH, Lu YY, Wang KZ (2006) Ruthenium(II) complex of hbopip: synthesis, characterization, pH-induced luminescence "Off-On-Off" switch, and avid binding to DNA. J Phys Chem B 110:2364–2371
11. Landge SM, Aprahamian I (2009) A pH activated configurational rotary switch: controlling the E/Z, isomerization in hydrazones. J Am Chem Soc 131:18269–18271
12. Schnarr NA, Kennan AJ (2005) pH-switchable strand orientation in peptide assemblies. Org Lett 7:395–398
13. Lee SB, Martin CR (2001) pH-switchable, ion-permselective gold nanotubule membrane based on chemisorbed cysteine. Anal Chem 73:768–775
14. Ceccacci F, Mancini G, Sferrazza A, Villani C (2005) pH variation as the switch for chiral recognition in a biomembrane model. J Am Chem Soc 127:13762–13763
15. Zimenkov Y, Dublin SN, Ni R, Tu RS, Breedveld V, Apkarian RP, Conticello VP (2006) Rational design of a reversible pH-responsive switch for peptide self-assembly. J Am Chem Soc 128:6770–6771
16. Yasutomi S, Morita T, Kimura S (2005) pH-controlled switching of photocurrent direction by self-assembled monolayer of helical peptides. J Am Chem Soc 127:14564–14565
17. Muller J, Glahe F, Freisinger E, Lippert B (1999) A major, pH-induced stereochemical switch of pairs of trans-oriented ligands in complexes of trans-a_2Pt^{II} (a=NH_3, CH_3NH_2). Inorg Chem 38:3160–3166
18. Xu H, Stampp SP, Rudkevich DM (2003) A pH switch in supramolecular polymeric capsules. Org Lett 5:4583–4586
19. Richmond CJ, Parenty ADC, Song YF, Cooke G, Cronin L (2008) Realization of a "lockable" molecular switch via pH- and, redox-modulated cyclization. J Am Chem Soc 130:13059–13065
20. Stepanov AS, Yanilkin VV, Mustafina AR, Burilov VA, Solovieva SS, Antipin IS, Konovalov AI (2010) Redox induced pH-switch of Tb(III) centered luminescence of Tb(III) complex, with p-sulfonatothiacalix[4]arene. Electrochem Commun 12:703–705
21. Tien P, Chau LK, Shieh YY, Lin WC, Wei GT (2001) Anion-exchange material with pH-switchable surface charge prepared by

sol-gel processing of an organofunctional silicon alkoxide. Chem Mater 13:1124–1130

22. Ramĩrez P, Mafé S, Alcaraz A, Cervera J (2003) Modeling of pH-switchable ion transport and selectivity in nanopore membranes with fixed charges. J Phys Chem B 107:13178–13187
23. Attakhova-Rohlfing D, Wark M, Rathouskŷ J (2007) Ion-permselective pH-switchable mesoporous silica thin layers. Chem Mater 19:1640–1647
24. Liu YL, Zhao MQ, Bergbreiter DE, Crooks RM (1997) pH-switchable, ultrathin permselective membranes prepared from multilayer polymer composites. J Am Chem Soc 119:8720–8721
25. Gao W, Song JF (2009) Polyaniline film based amperometric pH sensor using a novel electrochemical measurement system. Electroanalysis 21:973–978
26. Gao W, Song JF (2009) Towards surface acid–base property of the carboxylic multi-walled carbon nanotubes by zero current potentiometry. Electrochem Commun 11:1285–1288
27. van Hal REG, Eijkel JCT, Bergveld P (1996) A general model to describe the electrostatic potential at electrolyte oxide interfaces. Adv Colloid Interf Sci 69:31–62
28. Slim C, Ktari N, Cakara D, Kanoufi F, Combellas C (2008) Polyaniline films based ultramicroelctrodes sensitive to pH. J Electroanal Chem 613:139–150
29. Mažeikiené R, Tomkuté V, Kuodis Z, Niaura G, Malinauskas A (2007) Raman spectroelectrochemical study of polyaniline and sulfonated polyaniline in solutions of different pH. Vib Spectrosc 44:201–208
30. Kikas T, Ivaska A (2007) Potentiometric measurements in sequential injection analysis lab-on-valve (SIA-LOV) flow-system. Talanta 71:160–164
31. Lubert KH, Dunsch L (1998) The influence of protons on the impedance of polyaniline films. Electrochim Acta 43:813–822
32. Kocherginsky NM, Wang Z (2006) The role of ionic conductivity and interface in electrical resistance, ion transport and transmembrane redox reactions through polyaniline membranes. Synthetic Met 156:1065–1072
33. Wanekaya AK, Bangar MA, Yun M, Chen W, Myung NV, Mulchandani A (2007) Field-effect transistors based on single nanowires of conducting polymers. J Phys Chem C 111:5218–5221