Metal oxides based electrochemical pH sensors: Current progress and future perspectives

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ABSTRACT

Electrochemical pH sensors are on high demand in numerous applications such as food processing, health monitoring, agriculture and nuclear sectors, and water quality monitoring etc., owing to their fast response (< 10 s), wide pH sensing range (2–12), superior sensitivity (close to Nernstian response of 59.12 mV/pH), easy integration on wearable/flexible substrates, excellent biocompatibility and low cost of fabrication. This article presents an in-depth review of the wide range of MOx materials that have been utilized to develop pH sensors, based on various mechanisms (e.g. potentiometric, conductimetric, chemi-resistors, ion sensitive field effect transistor (ISFET) and extended-gate field effect transistor etc.). The tools and techniques such as potentiometric and electrochemical impedance spectroscopic that are commonly adopted to characterize these metal oxide-based pH sensors are also discussed in detail. Concerning materials and design of sensors for various practical application, the major challenges are toxicity of materials, interference of other ions or analytes, cost, and flexibility of materials. In this regard, this review also discusses the metal oxide-based composite sensing (active) material, designs of pH sensors and their applications in flexible/wearable biosensors for medical application are examined to present their suitability for these futuristic applications.

1. Introduction

Ion sensitive metal oxides (MOx) with micro- and nanostructured morphologies have gained increasing interest with potential applications in electrochemical-biomedical sciences and across numerous other scientific disciplines. Their unique electrical, electrochemical and biocompatible properties assert their utility in the fabrication of sensors for applications such as water and food quality monitoring, wearable systems for chronic diseases and industrial applications. With high surface to volume ratio, the MOx enhances the sensitivity, selectivity and catalytic activity. Further, the fast response and long lifetime in different environmental conditions, make MOx excellent candidates for the next generation of wireless sensing and online monitoring applications. Among various sensors used in these applications, the development of electrochemical pH sensors is one of the major implementations of MOx. The centrality of pH in a wide range of fields including chemistry, agriculture, food processing, pharmaceuticals, environmental science, chemical and biomedical engineering applications [1–8] also brings MOx to the forefront of materials research. The measurement and control of hydrogen ion concentration, represented in terms of pH value, is essential for many chemical and biological reactions. The pH value can greatly influence the physiological, biological and medical state of a person [9–14]. For example, the pH at chronic wound sites changes from slightly acidic (pH 5.5) for a healthy skin to basic (pH 7.0–8.5) for wounded skin due to the

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presence of bacterial colonies and enzymes [1]. Regular monitoring of pH value of skin can be helpful in terms of detecting the pathogenesis of skin diseases such as irritant contact dermatitis, acne vulgaris, atopic dermatitis, etc. [4,5,15]. Various cellular processes and enzymatic reactions in the human body also depend on the pH value. Likewise, in food processing, the pH value carries the signature of protein denaturization, gelification, growth and mortality of microorganisms and the germination or inactivation of bacteria spores [16–19]. Furthermore, water pollution and industrial wastewater can be effectively monitored by measuring the pH value [2,20–22]. In water pollution determination, a stable measured pH in the range of 6.5 to 8.5 is essential to ensure good quality.

The advances in pH sensing technology have focussed on enhancing the sensitivity, operational life time, biocompatibility, rapid response in wider ranges of pH, cost-effectiveness and portability etc by using proper sensitive materials. Several MOx materials have been reported recently for the development of pH sensors in pollution monitoring [22–24], biological and food quality applications [10,16] as well as emerging application areas such as flexible and wearable systems [1,3,4,25–30]. Fig. 1 shows some examples of recently developed pH sensors based on MOx which are integral to our daily life. Considering that several parameters govern the performance of a pH sensor, and the emergence of MOx as key material for the development of these sensors, the systematic review of

Fig. 1. Various metal oxide based pH sensors – key methods for preparation of electrode materials and sensor fabrication, type of sensors, parameters for analysis and applications: (a) structural properties of few materials “Reprinted from Publication [38] with permission from Elsevier”, (b) “Reprinted from Publication [39] with permission from Elsevier”, (c) “Reprinted from Publication [25] with permission from Elsevier” (d)–(h) different types of pH sensors including potentiometric, chemi-resistive, ISFET, EGFET and interdigitated, and (i)–(l) applications of pH sensors wearable and food quality monitoring (i) with permission [3], (j) “Reprinted from Publication [40] with permission from Elsevier”. (k) with permission [41], (l) “Reprinted from Publication [42] with permission from Elsevier”.

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the MOx based pH sensor presented here will be helpful for further progresses in terms of fabrication and applications. In particular, it is crucial to investigate the ionic exchange between sensitive nanomaterial and electrolyte. The variation in ionic concentration and the pH value of a solution, significantly change the electrochemical properties including electrochemical potential, impedance and capacitance of the electrodes. In addition, the influence of microstructure, particle shape, size and surface morphology of MOx nanostructures (e.g. thin films, nanotubes, nanobelts, nanowires, nanorectangles, nanorods, etc., shown in Fig. 1a–c) on the electrochemical properties etc. are presented. Few review articles have discussed the state-of-art of research and progress in pH sensing so far with limited discussion. For example, Korostynska et al. [31] have discussed the development of polymer-based pH sensors and Yuqing et al. [32] have presented new technologies for the detection of pH. Likewise, Qin et al. [33] have reviewed the developments in microfabricated electrochemical pH sensors, including those for free chlorine sensors. Recently Alam et al. [34] have pointed out the importance of polymers and organic materials-based pH sensors for healthcare applications. Some review papers on MOx based sensors have also been published and these include the one by Voanu and Guth [35], where the solid-state pH electrodes using MOx have been discussed. The pH sensing performance and properties of metal-MOx and MOx based pH sensors are described by Glab et al. [36]. The ion exchange sensing mechanisms of MOx pH sensors have been reviewed by Kurzweil [37]. The discussions in these review papers are limited to different materials and designs of pH sensors (Fig. 1d–h), the comparative study of fabrication methods and the sensing mechanisms. A substantial discussion is needed on different classes of pH sensitive MOx materials, to provide an accelerational impact on the research and development of novel miniaturized pH sensors for real-time monitoring in extreme high temperature/pressure and aggressive chemical environments, as well as for flexible/wearable applications (Fig. 1i–l). In this review article, we address these gaps and present a comprehensive and perspective analysis of electrochemical MOx based pH sensors. The elaborate discussion in this review includes various materials and types of pH sensors, and the analysis of sensing mechanism with different detection techniques including electrochemical impedance spectroscopy (EIS) analysis for material investigations.

This review is organized as follows: Section 2 briefly compares major types of electrochemical pH sensors and highlights the case for MOx based sensors. Various detection techniques and categories of MOx pH sensors such as potentiometric, conductimetric/chemi-resistors, ion sensitive field effect transistors (ISFET) and extended-gate field effect transistors (EGFET) are presented in Section 3. Important characteristics of pH sensors are mentioned in Section 4. In Section 5 we provide the sensing mechanism of MOx based pH sensors. The detailed description and comparison of various pH sensitive MOx materials in terms of fabrication, merits/demerits, performance and applications are described in Section 6. In Section 7, we discuss the challenges and future prospects of MOx pH sensors including their applications in food processing, pollution monitoring, wearable/flexible systems and extreme environments. Finally, the conclusions are summarized in Section 8.

2. Electrochemical pH sensors

The past few decades have witnessed a considerable effort in terms of the development of electrochemical (potentiometric, conductimetric, capacitive, and resistive) and non-electrochemical (including calorimetric and optical) pH sensors [30,43–51] for various applications. The sensitive electrodes (SE) which is a major component of any electrochemical pH sensor are mainly based on the glass membrane electrodes, MOx, metal/MOx, polymers and carbon. A comparison of SEs from these materials (Fig. 2) shows that ion sensitive MOx based on micro and nano structures received great interest. Electrochemical methods are the most widely adopted techniques for pH sensing. Many materials and designs have been investigated for the development of SEs for such sensors. The advantages and disadvantages of the most popular SEs implemented for the fabrication of electrochemical pH sensors are compared in Fig. 2. It is evident from Fig. 3 that the conventional glass based sensors have been popular for the pH measurement. However, mechanical fragility and the lack of flexibility/bendability hinder their implementations in emerging areas such as wearable systems. Further, durability and performance instability at high temperatures and pressures limit their use for pollution monitoring and other industrial applications. These drawbacks of glass-based sensors have encouraged researchers to explore alternative ways in pH sensing. Among these, MOx based pH sensors have attracted significant attention due to their high sensitivity (close to Nernstian response), fast response time (< 10 s), long life time (> 1 year), ease of miniaturization, stability in different atmospheres and biocompatibility of majority of MOx.

3. Metal oxide based pH sensors and detection techniques

The significance of MOx as sensitive electrodes for pH sensors fabrication and their sensing mechanisms was first highlighted by Fog and Buck [52]. Until now, various MOx have been used for the fabrication of pH sensors, among which Pt-group oxides, such as RuO2 and IrO2, have received the greatest attention owing to their remarkable sensitivity to hydrogen ions and high degree of accuracy. There are only few reports which utilized PtO2 as a pH sensor. According to Fog and Buck [52], the PtO2 based pH sensor shows a sensitivity of 46.7 mV/pH in the range 2–12 and hysteresis effect for pH 2-12-2 loop is ± 100 mV. Furthermore, certain other transition MOx, perovskite materials and mixed oxides such as Ta2O5, TiO2, SnO2, CeO2, WO3, Bi2O3-Nb2O5, PbO2, IrO2-TiO2, RuO2-TiO2, perovskite lithium lanthanum titanate (LLTO), yttria stabilized zirconia (YSZ), molybdenum oxide bronzes, etc. are investigated for pH sensor applications (discussed in following sections). In addition to this, some works have been done in the area of metal/ MOx based pH sensors such as those based on antimony and bismuth and the redox equilibrium between the metal/MOx phases (e.g. Sb-Sb2O3) attributes to the origin of their pH sensitivity [36,37,53,54]. However, the performance of such systems in pH measuring is limited because they are undesirably sensitive to several reduct agents and exhibit a systematic deviation from the expected behavior. To overcome these issues, many efforts have focused on the design of thin and thick MOx films on the top of non-conductive substrates and studying their suitability for a wide range of applications.
The sensitivity of the MOx pH sensor significantly depends on the type of material composition (Section 6 describes different types of MOx) and the deposition method since both these factors could influence the microstructure, porosity, surface homogeneity and crystalline structure of the material. This leads to variation in sensitivity of electrodes. Generally, the sensitivity of the pH sensors is expressed in terms of Nernstian response. If the sensitivity factor lies close to the ideal Nernstian response (59.14 mV/pH at 25 °C derived from the Nernst equation), the sensor is expected to show excellent performance. Fig. 3 summarizes various MOx based SEs which show sensitivity factors close to the ideal Nernstian response. We investigated the sensitivity of different MOx including IrO₂ [40,52,55–57], RuO₂ [22,52,58–60], TiO₂ [52,61–64], SnO₂ [52,65–68], Ta₂O₅ [52,69–71], WO₃ [72–76] and ZnO [77–81] and compared with the theoretical sensitivity at 25 °C derived from the Nernst equation (59.14 mV/pH), as shown in Fig. 3a. Fig. 3b represents the variation in sensitivity of the sensors of different materials fabricated by screen printing [22,23,59,60,82], sputtering [58,64,65,71], sol-gel [40,61,83–85] and electrodeposition [56,57,72] methods. In addition to this, the fabrication steps and mode of operation leads MOx based SEs into a different class of electrochemical pH sensors as discussed in the following section.

MOx based pH sensors are mainly categorized as: potentiometric, conductimetric/inductive/capacitive, chemi-resistive and ISFETs [33,86–88] or transistors based sensors [33,89,90]. In this section along with different types of pH sensors, we describe major techniques used to understand their working mechanisms such as potentiometry, cyclic voltammetry [37,84,91] and EIS [38,69,70,92–96].

### Glass Electrode
- **Advantages**
  - Very good pH response (close to Nernstian behavior)
  - High accuracy
  - Excellent stability over wide pH range
  - Long lifetime (several years)
  - Low cross-sensitivity to other dissolved ions
  - Very useful for practical applications in laboratories
- **Disadvantages**
  - Large in size, difficult for miniaturization
  - Mechanical fragility and expensive
  - Chemical instability in corrosive systems and strong alkaline and acid (eg. hydrofluoric) solutions
  - Performance depends on high pressure and temperature
  - Requires frequent calibrations
  - Limitations in the food industry, biomedical field and for online monitoring applications

### Metal oxide
- **Advantages**
  - Very good sensitivity close to Nernstian response
  - Fast response and long lifetime
  - High accuracy and low interferences to other ions
  - Very low hysteresis, drift and optical effects
  - Low cost, easy maintenance and miniaturized size
  - Very good mechanical and chemical stability
  - The sensor can be stored in atmospheric conditions for a long time
  - Good performance in extreme conditions
  - Easy miniaturization for flexible/wearable systems
  - Compatible for online monitoring applications
- **Disadvantages**
  - Slow response in basic solutions (few materials)
  - Large drift, hysteresis and optical effect (especially some ISFET based sensors)
  - Some materials show low accuracy and resolution
  - Some materials show super-Nernstian or sub-Nernstian response

### Polymer or Carbon
- **Advantages**
  - Very good flexibility of the sensor
  - Stretchable and bendable sensors
  - Applicability different type of substrate (cloth, paper, polymer, plastic etc.)
  - Low temperature processing
  - Conducting polymers exhibit high conductivity and electroactivity
  - Non conductive polymers have high selective response and high impedance which eliminates interference from other ions
  - Biocompatible for biosensors applications
- **Disadvantages**
  - Limited pH sensing range
  - Low reproducibility, reusability and long life time
  - Poor reliability due to defects such as pinholes in some films and adhesion problems
  - Poor mechanical and chemical stability

### Metal/Metal oxide
- **Advantages**
  - Small and rugged sensors
  - Easy for miniaturization
  - Mechanically and chemically stable
  - Applicable for low impedance measuring systems
  - Relatively stable and insensitive to salt concentration
  - Useful for measuring body fluids such as those from gastrointestinal tracks
- **Disadvantages**
  - Limited pH sensing range
  - Sensitive to several redox agents and oxygen pressure above the test solution
  - Systematic deviation from Nernstian behaviour
  - Poor resolution, repeatability and stability for polycrystalline electrode
  - Very sensitive to several ligands and components of standard buffers
  - Not ideal for blood monitoring

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**Fig. 2.** Comparison of the major materials used for electrochemical pH sensor fabrication.
3.2. Capacitive/conductimetric/inductive based pH sensor

A capacitive/inductive/conductimetric pH sensor exploits changes in electrical properties such as capacitance or impedance of a film deposited on interdigitated electrodes (IDE) in response to the electrochemical reaction occurring at the solution-SE interface.
The majority of conductimetric pH sensors have IDE structure and operate without RE [31,92–94,109–111]. A planar IDE based sensor is a simple two electrode probe configuration of an electrochemical cell setup and is widely used for miniaturized applications of sensors, transducers and actuators [92,109,112–116]. The conductimetric method is easy and less expensive as compared to any other method. As shown in Fig. 4d, the fabrication of conductimetric/capacitive pH sensors is simple and cheaper than any other method involving two basic steps - deposition of IDE on a substrate and deposition of the sensitive layer. Screen printing has been widely used for depositing the conducting electrode and the SE on the substrate [31,69,93,109,111]. IDE based structure allows mass production of sensors with miniaturized size, well defined geometry, compactness and sensitivity. Even though this type of sensor has several advantages, due to the possible degradation by long-term operation in different biological and chemical conditions, its
applications are limited. Moreover, the conductivity of solution has a significant influence on the sensing performance of MO_x based conductimetric sensors [69,101]. Polymer based conductimetric sensors have been widely used for biomedical applications [31]. The electrochemical reaction at MO_x- solution interface of an IDE based pH sensors can be investigated by using EIS analysis.

The EIS analysis is a non-destructive steady-state method and is used for analyzing a complex electrochemical system over a broad range of frequencies for sensors, batteries and supercapacitors [3,92,117–121]. This technique enables measuring the response of a circuit or an electrochemical system and is useful in elucidation of the sensing mechanism of a MO_x pH sensor by getting insight into phenomena, such as adsorption, ion exchange, charge transfer, diffusion, etc. [38,70,92,93,96,119,120]. One of the best designs of a sensor with two electrodes configurations for EIS analysis is the one with an IDE structure [92,109]. In impedance spectroscopic data analysis, the features of an investigated system can be portrayed by using Nyquist and Bode plots (Fig. 4e). These plots are useful to analyze conventional electric circuits and the equivalent circuits to describe electrochemical properties of the electrodes and their interaction with a solution. The Bode plot reveals the capacitive, resistive and inductive features of the electrochemical system. In most of the electrode-solution interface reactions, the variation in impedance of a Faradaic reaction may be due to (1) adsorption of reacting species (2) diffusion of ions or (3) both adsorption and diffusion processes together [119–121]. In addition to Faradaic reaction, electrochemical double layer (edl) may also develop during-electrode-solution reaction. These phenomena may be related to the contribution of electrolyte, the electrode-solution interface, the nature of the material and electrochemical reaction occurring on the electrode. In our work, we observed from the EIS analysis of IDE based pH sensors that the sensing mechanism of thick film RuO_2 based pH sensors can be attributed to a combination of electron transfer and ion exchange processes at the solution/MO_x interface as illustrated in Fig. 4e. In the high-frequency range, the conductivity and charge transfer processes depend on the solution and sensing layer properties are dominant. However, in the low-frequency range, ion exchange (adsorption/diffusion) processes prevail and sensor characteristic strongly depends on the solution pH. The ion exchange processes also depend on the material properties, like structure, composition, porosity and surface homogeneity [92,93].

3.3. Chemi-resistive/Conductimetric pH sensor

The chemi-resistor and conductimetric based MO_x pH sensors work by similar principle and they do not require a RE for their operation. In chemi-resistor pH sensors, the SE deposited between the two conducting electrodes is shown in Fig. 4f. The pH sensitive semiconductor nanomaterials are mainly used for fabrication of chemi-resistor pH sensors. In this type of pH sensors, the change in H_3O^+−/OH^− ions in the solution generates a change in electrical properties, in particular changes in resistance and conductance of the SE material [33]. The sensing performance of a chemi-resistor based pH sensor is strongly dependent on the degree of protonation. There are only few reports on chemi-resistive based pH sensor with MO_x as SE [122]. It was found that for TiO_2 nanowires (NW) based chemi-resistive pH sensor with increasing pH from acidic to basic, the conductance value deceases linearly with a resolution of 5.68 ± 0.28 nS/pH [123]. The decrease in conductance is due to the reduction and increases in the depletion layer at the surface of the TiO_2 NWs from reacting with H^+/OH^- ions. For operating the chemi-resistive sensors, an external power supply is often required. To overcome the need for bulky power sources, we have reported a CuO based self-powered flexible chemi-resistive pH sensor. For this self-powered application, a flexible solar cell was used as an energy generator and a flexible graphene foam based supercapacitor was applied as an energy storage device [3]. In addition to the MO_x, there are few other reports on graphene and CNTs based chemi-resistor pH sensors [89,90].

3.4. Ion-sensitive field effect transistor (ISFET) pH sensor

ISFET is a type of potentiometric device which operates similarly to metal oxide field effect semiconductor transistor (MOSFET) [124] (shown in Fig. 4g). In 1970, Bergveld [88] used the first ISFET for measurements of ion activities in electrochemical and biological environments. In ISFET, the gate is covered with an ion-sensitive layer and is placed between the source and drain (Fig. 4g). The current flowing between source and drain is controlled by the electrostatic field generated by the gate. In this method, instead of measuring the potential difference between the two sides of the glass membrane, the current passing through the transistor is recorded. The wide range of materials used for making ion-sensitive layers on a gate includes ceramics, organics, polymers or catalytic metal layers [33,68,71,87,88,124]. The pH sensing mechanism of the oxide surface of a gate electrode can be described by the site binding theory [125]. A detailed review of ISFETs as pH and biosensors is beyond the scope of this article as it has been made available previously, for example those by Nakazato [126] and Lee et al. [127].

ISFETs can be easily adapted to a broad range of chemical, biomedical and biochemical measurements [28,124] and as compared with glass pH sensor, they have many advantages including miniaturized size, low cost, and fast response. Since ISFETs are directly formed on the FET electrode, they also have several disadvantages such as device instability, low current sensitivity and sensitivity to light, etc. [33]. The optical effect, hysteresis, and drift are the three non-ideal characteristics observed in ISFET based pH sensors. To overcome these drawbacks, Spiegel et al. [128] introduced EGfET, where FET is isolated from the chemical solution as the sensitive film is deposited at the end of signal line extended from the FET electrode [129,130], as illustrated in Fig. 4h. EGfETs are widely used for biosensor applications [128–132] and their major advantages are long-term stability, insensitivity to light and temperature drift, and disposability. The pH sensing mechanism of EGfET can be described by site binding theory. Only few semiconductor MO_x (e.g. SnO_2 on FTO substrate [133], ITO [134]) were utilized for EGfET based pH sensor fabrication [135,136]. In addition to ISFET and EGfET, recently there are many reports on the fabrication of chemi-transistor and electrolyte gated field effect transistor (EGfET) and reparable extended gate ion-sensitive field-effect transistor (SEGfET) based pH sensors [137]. Organic semiconductors are mainly used for the development of chemi-transistor and EGfETs based pH sensors [33]. Qin et al. [33] recently reported a detailed
comparative study of the structure and operating mechanism of such type micro-fabricated electrochemical pH sensors.

4. Characteristics of pH sensor

The performance of the pH sensor is determined by their response time, stability, selectivity, interference of other ions and non-ideal effects such as hysteresis and drift. These characteristics, which depend on many parameters, of the metal oxide-based pH sensor is discussed in the following sections.

4.1. Response time

The response time of a solid state potentiometric pH sensor is defined as the time ($t_{90}$) required for its open circuit potential (OCP) or electromotive force (emf) to reach 90% of an equilibrium value after immersing the sensor in the solution of a given pH value \[38\]. In order to analyze the response time of the sensor, the pH value is drastically changed from the acidic to the basic solution and vice versa, and the output potential is measured. The response time of a MOx pH sensor depends on many factors related to the SEs, including the composition, structural properties, morphology, thickness, and pore size. The response time of the sensor also depends on measurement range of pH value. Most of the sensors show a faster response time in the acidic region as compared to alkaline solution. As an example, potential–time curves of IrO$_2$-rGO based sensor in buffer solution at different pH value are shown in Fig. 5a \[138\]. At an acidic pH of 4, the sensor shows faster response time (150 s) than the sensor in a basic solution of pH value 12 (200 s). In any case, the response of the sensor in neutral pH region is much slower than in both the acidic and basic regions \[138\]. In comparison to acidic and basic solutions, the fastest response of the sensor in acidic solutions is related to ion exchange of small mobile H$^+$ ions, dominant in acidic solutions. In our previous work on RuO$_2$-Ta$_2$O$_5$ based sensor, we also have observed that in the acidic region of solution, the sensor exhibited a much shorter response time ($< 8$ s), than in basic solutions ($< 15$ s). This faster response is related to H$^+$ diffusion which is dominant in acidic solutions \[23\].

The method of fabrication changes the morphologies and surface properties of materials, which also influences the response time of pH sensors. As an example, Zhuiykov et al. \[39\] observed that, for planar thick film Cu$_2$O doped RuO$_2$ SEs, the response time to pH changes was strongly dependent on the electrode thickness, decreasing from $\sim 80$ to $120$ s for a SE thickness of $\sim 2$ μm to $\sim 25$ s for a thickness of $\sim 5$ μm \[39\]. These changes in response time are due to the surface electrochemical reaction associated with the grain size and grain faceting of the SE present in the “inner” active surfaces of the SE (shown in Fig. 5b), and the increase in open porosity with increasing thickness. When a solution reacts on this surface of the MOX layer, three complex interfaces will be formed (i) outer surface: the MOX SE/solution macro-boundaries (ii) inner surface: the MOX SE/solution micro-boundaries due to penetration of the ions in the liquid into pores and inter-grain regions and (iii) the oxide SE layer/support Pt layer interface. For the faster response of the sensor, the first two regions are very significant. The ions from the outer active surface are diffused or adsorbed into the inner
active. To further investigate the surface morphologies of SE impact on response time, Zhuiykov et al. [39] compared the crystalline properties of thin and thick film SE. The thicker film presented higher porosity and larger grain size (1.5–2 µm) than the thin film (grain size 600 to 800 nm). The dimension of the inner active region of thick film is in the range of 50–110 nm. For this SE, the thicker film had presented faster response due to the well crystallized material.

Similarly, Xu and Zhang [38] found that the response time is less than 40 s for the pH sensitive electrodes based on RuO2 nanoparticles modified with vertically aligned carbon nanotubes (RuO2/MWCNT) deposited by magnetron sputtering [38]. Both, the nanostructured nature and porosity of the sensing film may improve the response time of the sensor. It is also observed that the sensor shows faster response in acidic solutions than in basic solutions, and this may be related again to ion exchange of small mobile H+ ions in the SE.

4.2. Interference effect/Selectivity

One of the major drawbacks of a MOx pH sensor is interference effect of other ions on the sensing performance. Several reactions may occur due to the presence of different ions in a solution - both in the acidic and basic pH ranges and this affects measured potential of the sensor. The selectivity coefficient of an ion SE characterizes the ability to distinguish a particular ion from others. According to International Union of Pure and Applied Chemistry (IUPAC) recommendation, the selectivity coefficient, $K_{\text{ex}}$, is evaluated by means of the emf response of ion-selective electrodes in mixed solutions of primary ion, A, and interfering or less desirable ion, B (Fixed Interference Method, FIM), in separate solutions of A and B (Separate Solution Method, SSM) [140]. The interfering impact of common anions (Cl−, Br−, SO42−) and cations (Li+, Na+, K+, Ca2+) is usually insignificant in majority of MOx based pH sensors [23,37,82]. However, from the literature it is clear that the SEs made of commercial pastes show susceptibility to interferences caused by common anions such as halide, sulphate, carbonate ions due to the presence of lead in the SE [139]. The influence ions in sensor performance purely depends on type of materials and concentration of ions in the solution.

4.3. Drift effect

Drift effect refers to the slow non-random change of output voltage of the SE with time in a solution with constant composition and temperature. The drift rate increases while increasing the pH value of solution from acidic to basic. Bousse and Bergveld [141] suggested that presence of OH− ion is one of the factors that causes the observed higher drift in alkaline solutions than in acidic solutions [65,141]. According to Zhuiykov [59], the RuO2 sensing electrode shows a voltage drift during the initial month of testing. This is due to the H+ transport through SE which is governed by H2 trapping at the trap site existing at the grain boundaries or micro- pores of the nanostructured SE [59]. The drift in potential also depends on the experimental temperature; when temperature is high, pH-response drift is significant for the first few days and thereafter stabilized very fast. Even though the method of deposition of SE is similar, the sensors may exhibit different drift rates [65]. The drift effects of few MOx materials are presented in the Table 1. Table 1 reveals that, several factors such as the measurement circuit, quality and composition of the SE, type of materials, thickness, surface homogeneity and porosity of the sensitive layer significantly influence the drift effect.

| Materials | Method of fabrication | Drift Effect |
|-----------|----------------------|--------------|
| RuO2      | radio frequency sputtering | pH 4: 0.13 mV/pH; pH 7: 0.38 mV/pH; pH 10 7.31 mV/pH |
| RuO2      | screen printing | ± 1.5 mV/month (after 15 days of measurement) |
| IrO2      | electrodeposition | pH 1: 0.02 pH/h; pH 7: 0.003 pH/h; pH 11: 0.07 pH/h |
| IrO2      | sol–gel | 3–10 mV |
| Ta2O5     | radio frequency sputtering | pH 7: 0.03–0.05 mV/day |
| Ta2O5     | electron-beam evaporation | pH 7: < 0.5 mV/h (after 3 h); 0.2 mV/h (after 10 h) |
| WO3       | radio frequency sputtering | pH 1: 1.5 mV/h; pH 3: 3.6 mV/h; pH 5: 6.6 mV/h; pH 7: 15.7 mV/h |
| WO3       | magnetron sputtering | < 3 mV |
| TiO2      | sol–gel | pH 7: 1.97 mV/h |
| TiO2      | radio frequency sputtering | 1.67 mV/h |
4.4. Hysteresis effect

The memory or hysteresis effect arises when a pH electrode which has been used several times in the same pH buffer solution leads to random output voltages [58,102]. The hysteresis width in acidic region of solution is smaller than in alkaline solution since the diffusion speed of $H^+$ ions is faster than $OH^−$ ions. One of the interesting observations in MOx based sensors is the dependence of hysteresis width on measurement loop time. It was found that the hysteresis width increases with increasing loop time [65]. Few reports on hysteresis and new materials and methods indicate that the hysteresis effect is lower in the case of MOx pH sensors. For comparison, corresponding to the hysteresis widths observed in different pH sensors based on MOX, we investigated the measured potential value for different loop values and a few of them are presented in Table 2. Hence, the hysteresis width of MOx pH sensor strongly depends on the pH measurement loop and time of measurements, the surface area and crystalline properties of the materials.

5. Sensing mechanism

Researchers have invested considerable effort on identifying the sensing mechanism of MOx based pH sensors. Five different mechanisms considered by Fog and Buck [52] to explain pH sensitivity of MOx include: (i) simple ion exchange in a surface layer containing $–OH$ groups, (ii) a redox equilibrium between two different solid phases, (iii) redox equilibrium involving only one solid phase whose hydrogen content can be varied continuously by passing current through the electrode, (iv) single phase ‘oxygen intercalation’ of the electrode and (v) a steady state corrosion of the electrode material. Among these, the ‘oxygen intercalation’ is found to provide closest explanation for mechanism for pH sensitivity [139]. Following the explanation by Fog and Buck [52], Trasatti [146], Mihell and Atkinson [147] have also suggested that the pH response could be due to ion exchange in surface layer containing $–OH$ groups. In general, when the sensor comes into contact with a solution, the MOx surface gets covered by hydroxide groups due to dissociative adsorption of water. The oxide sites formed by releasing protons can result in formation of a couple of higher and lower valency MOx and lead to generation of a potential difference between the SE and RE. The magnitude of this potential is proportional to pH of the solution according to the Nernst equation [37]:

$$E = E_0 - \frac{2.303RT}{nF} \cdot pH$$  \hspace{1cm} (1)

where $E$ is electromotive force (emf) of the electrochemical cell, $E_0$ is standard potential, $R$ is universal gas constant, $T$ is absolute temperature, $n$ is the number of electrons and $F$ is Faraday constant. At temperature $T$ equal to 25 °C and for one electron electrode reaction, the slope factor of the plot is 59.14 mV/pH.

As per site-binding theory [61,148,149], after immersion in an aqueous solution, formation of surface groups $–O−$, $–OH$ and $–OH_2^+$ occurs for a majority of oxides, as illustrated in Fig. 6a. Protons and hydroxide ions from the solution get attracted to oxygen ions from the MOx crystal lattice and to the surface cations, respectively. This results in the covering of MOx by hydroxide groups. The created metal hydroxide groups can donate a proton to the solution and form a negative surface group or accept a proton from the solution converting into a positive surface group [61,70,148,150]. The charged surface groups at the MOx- solution interface create

| Materials | Method fabrication | pH loop/values | Hysteresis (mV) | Ref |
|-----------|--------------------|----------------|----------------|-----|
| RuO₂      | radio frequency sputtering | 7-4-7-10-7 | 4.36 | [58] |
| RuO₂      | magnetron sputtering | 7-4-7-10-7 | 2.2 | [38] |
| IrO₂      | sol-gel | 1.50, 2.81, 3.75, 6.28, 7.86, 9.52 and 10.50 | 23.7, 9.5, 0.3, 14.5, 16.5, 6.7, and 11.5 | [40] |
| IrO₂      | Electrodeposition | 2-10-2 | 2.5 ± 0.6 | [56] |
| IrO₂      | electrodeposited | 7 | 1.5-0.5 | [57] |
| WO₂      | magnetron sputtering | 2-12 | < 13 | [73] |
| WO₂      | radio frequency sputtering | 3-1-3-5-3 | 7.2 | [143] |
| Ta₂O₅     | radio frequency sputtering | 7-4-1-4-7-10-7 | −5 | [70] |
| Ta₂O₅     | electron-beam evaporation | 3-10 | 1.5-9 | [142] |
| SnO₂      | radio frequency sputtering | 7-10-7-4-7 | < 3 | [145] |
| SnO₂      | sol-gel | 5-1-5-9-5 | 3.74 | [83] |
an edl structure, as shown in Fig. 7b. The edl consists of the Helmholtz layer (compact layer) and the diffuse layer (Stern layer). The Helmholtz layer contains inner Helmholtz plane (IHP) and outer Helmholtz plane (OHP), as illustrated in Fig. 6b. The charged surface groups are located in IHP and are strongly adhered to MOx surface by chemical bonding. In OHP, the ions from the solution are attracted to the surface charge by Coulombic interaction. In the diffuse layer, ions in the solution move freely due to thermal or electrical forces \[92,148,149\]. These reactions may occur due to the involvement of diffusion of ions, adsorption of ions or be related to both diffusion and adsorption of ions at the MOx surface \[70,92\].

A change in the pH value of a solution affects the equilibrium state of MOx surface, which may lead to changes in electrical properties and surface potential \(\Psi\) of the SE \[61,92,109,151,152\]. The variation in electrical properties of edl depends on the nature of electrode material and its chemical reactivity at the solution interface. To investigate the sensing mechanism of pH ISFET, Liao et al. \[61\] carried out detailed experimental and theoretical study based on site binding theory at the point of zero charge pH\(_{PZC}\) and surface potential of a tin oxide gate ISFET. The changes of \(\Psi\) of MOx can be described as \[61\]:

\[
2.303(\text{pH}_{\text{PZC}} - \text{pH}) = \frac{q\psi}{kT} + \sinh^{-1}\left(\frac{q\psi}{kT\beta}\right)
\]

where \(\beta\) reflects the sensitivity of the gate insulators and depends on the surface density of hydroxyl groups.

\[
\beta = \frac{2q^2N_s(K_aK_b)^{1/2}}{kTC_{DL}}
\]

Here, \(K_a\) and \(K_b\) are dissociation constants related to acidic and basic equilibrium, \(N_s\) is the total number of surface sites per unit area. The pH sensitivity is higher, and the response is more linear when \(N_s\) is larger. The value of \(N_s\) depends on the crystalline structure of material. \(C_{DL}\) is a double layer capacitance derived from the Gouy–Chapman–Stern model.

6. Overview of different metal oxides for pH sensor fabrication

6.1. Ruthenium oxide (RuO\(_2\)) based pH sensors

RuO\(_2\) is a versatile and attractive MOx which finds applications in electrochemical sensors, electrocatalysis and supercapacitors \[52,150,153\]. RuO\(_2\) is a mixed electronic ionic conductor with the stable rutile structure. Compared to other pH sensitive metal oxides, RuO\(_2\) based pH sensors have been found to exhibit outstanding sensing performance over wide pH ranges (2–12) due to their chemical stability and high conductivity which inhibit the space charge accumulation. Their significant advantages over the conventional glass pH electrode and other MOx based pH electrodes include high sensitivity, fast response, long lifetime, low sensitivity to interferences caused by different ions, negligible hysteresis effect, and excellent repeatability (some of the features are mentioned in Tables 1, 2 and 3). Fog and Buck \[52\] suggested two main reasons for pH response in RuO\(_2\) metal oxide – “oxygen intercalation” and ion exchange in a surface layer containing –OH groups. McMurray et al. \[139\] and Trasatti \[146\] have also confirmed this mechanism. There are many studies which have reported the use of RuO\(_2\) alone or combined with other oxides for pH sensitive electrodes. Several methods, including thick film technology, have been employed for RuO\(_2\) based pH sensor fabrication.
McMurray et al. [139] reported a pH sensor with RuO2·xH2O-lead borosilicate glass composite as a sensing material. The sensor with RuO2: glass ratio of 1:1 shows near-Nernstian potential in the pH range 2–12 with response time about 90 s and maximal hysteresis of 30 mV. It was noted that higher glass content in the SE causes smaller open porosity. This leads to decrease in the

Fig. 7. Schematic view and microscopic images of the (a) RuO2 based pH sensors (I) conductimetric, (II) potentiometric, “Reprinted from Publication [102] with permission from Elsevier”. (b) representation of impedance spectroscopic analysis explaining the diffusion, charge transfer and solution resistance of the RuO2 based pH sensor. (c) and (d) SEM and TEM images of the RuO2/MWCNTs nanocomposite, “Reprinted from Publication [38] with permission from Elsevier”. (e) pH response curves with different immersion time in pH 7 buffer solution, “Reprinted from Publication [38] with permission from Elsevier”, (f) the effect of time on potential and sensitivity of the RuO2/MWCNTs electrode in buffer solutions “Reprinted from Publication [38] with permission from Elsevier”. (g) response/recovery time for both freshly prepared Bi2Ru2O7+x + RuO2-SE and after use for 12 months “Reprinted from Publication [159] with permission from Elsevier”. (h) potential vs. pH of thick film electrode of ruthenium oxide in presence of Cl− (□), Br− (○), SO42− (▲) and NO3− (+) “Reprinted from Publication [82] with permission from Elsevier”. (i) multi-sensor for water quality monitoring “Reprinted from Publication [2] with permission from Elsevier”. (j) 3D printed pH sensors, RuO2 working electrode (left) and RuO2-PVB-SiO2 reference electrode (right) “Reprinted from Publication [42] with permission from Elsevier”.

[20,59,60,154,155].
Table 3
Methods of fabrication and properties of MOx based electrochemical pH sensors.

| Materials                        | Fabrication method                        | pH range | Sensitivity (mV/pH) | Response Time | Ref.       |
|----------------------------------|-------------------------------------------|----------|---------------------|---------------|------------|
| RuO2                             | RF sputtering                             | 1-13     | 55.64               |               | [58]       |
| Pt-doped RuO2                    | Screen printing                           | 2-13     | 58                  | 1-2 s         | [59]       |
| RuO2-TiO2                        | Pechni method                             | 2-12     | 56.03               |               | [84]       |
| RuO2-TiO2                        | Screen printing                           | 2-12     | 56.11               | < 15 s        | [60]       |
| Bi2RuO2+RuO3                     | Screen printing                           | 2-13     | 58                  |               | [159]      |
| RuO2-commercial paste            | Screen printing                           | 4-11     | 57                  |               | [82]       |
| RuO2-commercial paste            | Screen printing                           | 1-12     | 57 ± 3              | < 5 s         | [22]       |
| Ni-RuO2                          | Thermal decomposition                     | 1.5-12.5 | 52 ± 2              |               | [228]      |
| RuO2-H2O: Glass mixture          | Hand painting                             | 2-12     | 59                  |               | [139]      |
| RuO2-commercial paste            | Screen printing                           | 2-10     | 52.1                |               | [22]       |
| Graphite based ink with 9.8% RuO2 (disposable pH sensor) | Screen printing | 2-9       | 51                  |               | [160]      |
| RuO2 nanoparticles-MWCNT         | Magnetron sputtering                      | 2-12     | 55                  | < 40 s        | [38]       |
| RuO2-SnO2                        | Screen printing                           | 2-12     | 56                  | < 8 s and < 15 s in acidic and basic solution. | [23]       |
| RuO2-TiO2                        | Screen printing                           | 2-12     | 56.5 ± 0.7          | < 5 s and 9 s, for acidic to basic and basic to acidic solution changes | [102]      |
| IrO2 (flexible sensor)           | Dip coating                               | 1.5-12   | 51.1                |               | [40]       |
| IrO2                             | Carbonate melt oxidation                  | 1-13     | 58.4 ± 0.2          |               | [55]       |
| IrO2-TiO2 (30-70) mol%           | Pechni method                             | 1-13     | 59.1 ± 1.47         | 120 s · pH 4-12, 10 s · acidic region, 5 s · basic region | [85]       |
| IrO2                             | Electrodeposition                         | 3-11     | 72.9 ± 0.9          |               | [57]       |
| IrO2                             | Anodic electrodeposition                   | 2-10     | 63.5 ± 2.2          | 0.5, 1.5, and 1 min for pH regions 5, 5-7, and > 7 | [56]       |
| Ta2O5                            | Sputtering                                | 2-12     | 58-59               | < 0.3 s       | [71]       |
| Ta2O5-EIS                        | Electron beam evaporation                 | 2-12     | 57 ± 1.5            |               | [142]      |
| Ta2O5                             | Screen printing                           | 2-10     | 45                  |               | [69]       |
| Ta2O5-EIOS                       | Sputtering and thermal oxidation          | 1-10     | 56.19 ± 2           |               | [70]       |
| SnO2/Al                          | Sputtering                                | 2-10     | 58                  |               | [67]       |
| SnO2/EGFET                       | Hydrothermal method                       | 1-13     | 55.18               |               | [181]      |
| SnO2                             | RF sputtering                             | 2-12     | 58.1                |               | [65]       |
| SnO2/ITO                         | RF sputtering                             | 2-12     | 59.9 ± 1.037        |               | [66]       |
| TiO2                             | MOCVD                                     | 1-13     | 57.4-62.3           |               | [62]       |
| TiO2                             | Spin coating                              | 1-11     | 58.73               |               | [61]       |
| TiO2 nanotube array modified Ti electrodes | Anodization of Ti substrate electrode | 2-12     | 54.6                | < 30 s        | [63]       |
| TiO2 and Ru doped TiO2 (TiO2/Ru) | Co-sputtering                             | 1-13     | 37.73 · TiO2 · Ru   |               | [144]      |
| WO3/MWNT                         | Magnetron sputtering                      | 2-12     | 41                  | < 90 s        | [73]       |
| WO3                              | RF sputtering                             | 1-7      | 44.85, 47.90, 50.10, 52.85, and 55.80 at 25, 35, 45, 55, and 65 °C respectively | [143]      |
| W/WO3                            | Electro oxidation                         | 2-12     | 53.5 ± 0.5          | For pH 6-7- 3 s, For high pH 15 s | [74]       |
| Amorphous WO3                    | RF sputtering                             | 1-7      | 50                  |               | [212]      |
| CeO2                             | Screen printing                           | 7.2-10.8 | 58 ± 4 · CeO2 ± 4  |               | [212]      |
| Ce9aSm5bO2                        | Screen printing                           | 7.2-10.8 | 40 ± 4 · Ce9aSm5bO2 |               | [212]      |
| Ce9aZr5bO2                        | Screen printing                           | 7.2-10.8 | 51 ± 2 · Ce9aZr5bO2 |               | [212]      |
| PbO2                              | Transformation into α-PbO2 and β-PbO2 by oxidation in alkaline and acidic solutions | 1-12     | 57.96 · α-PbO2 57.80 · β-PbO2 | [223]      |
| PbO2                              | Electrodeposition                         | 1.5-12.5 | 64.82 · α-PbO2 57.85 · β-PbO2 | 1 s and < 30 s in acidic medium and in alkaline solutions | [214]      |
| PbO2 based graphite epoxy        | PbO2-graphite epoxy composite was inserted into the glass tube. | 1-11     | 58.7 ± 0.3 and 60.8 ± 0.2 in aqueous and aqueous ethanolic solutions | < 15 s | [229]      |

(continued on next page)
The doping of RuO₂ or mixing with other oxides improves the sensing performance of RuO₂ based pH sensors. The pH sensor with nanostructured Pt-doped RuO₂ electrode exhibits an excellent Nernstian response with a very fast response [59]. The use of binary MOₓ has been considered as one of the most effective methods for improving the electrocatalytic properties, sensing performance and stability of pH sensors [23,60,84,93,102]. The binary MOₓ are often utilized as dimensionally stable anodes (DSA) for various applications including chloro-alkali industry, water electrolysis, oxidation of organics, organic synthesis, etc. [156–158]. In the binary MOₓ system, an active transition oxide (RuO₂, IrO₂, etc.) is mixed with a chemically inert oxide, like Ta₂O₅, SnO₂, TiO₂, etc. The addition of inert oxides decreases the cost and can improve the stability, electrochemical properties and service life of the electrodes [156–158].

We have reported the development of new thick film SEs based on binary MOₓ, such as RuO₂-TiO₂ [60], RuO₂-Ta₂O₅ [23,93,101] and RuO₂-SnO₂ [102] for potentiometric and conductimetric pH sensors, as shown in Fig. 7a. X-ray photoelectron spectroscopy (XPS) studies carried out for RuO₂-TiO₂ and RuO₂-Ta₂O₅ layers confirmed the dependence of the surface elemental composition on the pH value of a solution used for sensor treatment [60,93]. The degree of surface hydroxylation was proved to be correlated with pH change. Larger scale adsorption of hydroxyl groups and water at the surface was observed for the samples conditioned at pH of 4 and 10 as compared to those freshly prepared or conditioned in neutral water (pH = 7). The highest surface hydroxylation was found to occur for the alkaline solution (pH = 10). It was revealed that Ru ions in the sensing layer have different oxidation states (+4 and +6). Stabilization or creation of mixed oxide phases was observed at pH of 4 and 10 while neutral environment probably led to the dissolution of these phases [60]. The potentiometric measurements showed that thick film pH sensors with the RuO₂-rich sensing electrodes obey Nernstian behavior close to the theoretical value for the one electron electrode reaction. Thick film pH sensors based on RuO₂-TiO₂ [60], RuO₂-Ta₂O₅ [23] and RuO₂-SnO₂ [102] exhibit a very fast response, long lifetime, reproducibility, resistance to interferences caused by ions such as Li⁺, Na⁺ and K⁺ as well as low hysteresis and drift effect. The EIS analysis reveals that the capacitance, conductance, absolute value of impedance and phase angle of the conductimetric sensors in the low frequency range are strongly dependent on the pH value of a solution. The complex plane impedance spectra of the thick film IDE pH sensors based on RuO₂ [92], RuO₂-TiO₂ [60], RuO₂-Ta₂O₅ [93], and RuO₂-SnO₂ [102] indicate that the mixed electronic and ionic conduction underlies the sensing mechanism, as shown in Fig. 7b. This mechanism is more prominent for the sensors with sensing electrodes based on RuO₂ and binary oxide compositions with higher fraction (70 wt%) of RuO₂ [93,102]. The electrochemical sensing performances of pH sensors based on several binary MOₓ fabricated by different methods are compared in Table 3.

Xu and Zhang [38] developed a RuO₂/MWCNTs nanocomposites based sensor to monitor pH. RuO₂ was deposited on vertically aligned MWCNT by magnetron sputtering. The morphology of the obtained composite is shown in Fig. 7c and d which depict the uniform distribution of the tubular MWCNT (in SEM image) and a magnified view of the tubular cross section near the edge of a single tubular structure due to coating of RuO₂ (in TEM image), respectively. The freshly prepared sensor shows a sensitivity of 57 mV/pH as presented in Fig. 7e. However, after immersing the sensor in pH 7 buffer solution for 24 h the sensitivity is reduced to 55 mV/pH. The effect of immersing time on sensitivity and E₀ is shown in Fig. 7f. After 24 h of immersion in pH 7 buffer solution, the E₀ and sensitivity value were almost stable [38]. The observed initial drift in potential and sensitivity is due to the hydration reactions at the RuO₂ electrode surface and similar behavior was also reported by Zhuiykov [59] as well as in our previous work [60] on RuO₂ based pH sensors. Zhuiykov [159] developed a new sensing material based on Bi₂Ru₂O₇₋ₓRuO₂ for online monitoring of pH of water. The lead content in the commercial RuO₂ paste, pH sensing electrode often shows poor selectivity in the presence of halide, sulphate and carbonate ions in water. Application of this new material enabled the author to reduce the lead content and restrict its detrimental impact on the measurement results. It was also observed that in warm water, the sensor’s response to pH changes was much faster than in cold water (shown in Fig. 7g). The measurement (Fig. 7g) shows the response/recovery rates for the freshly prepared and the sensor used for 12 months. When the sensor was stored in water, the sensor response/ recovery rate is influenced by the biofouling effect. In the subsequent study, Zhuiykov et al. [39] investigated the influence of the thickness of Cu₂O doped RuO₂ electrode on the performance of pH sensor which we have already discussed in Section 4.1.

### Table 3 (continued)

| Materials     | Fabrication method | pH range | Sensitivity (mV/pH) | Response Time | Ref. |
|---------------|--------------------|----------|---------------------|---------------|------|
| MnO₂          | Solid state reaction | 2–12     | 78.3                | Few seconds in acidic and basic solutions | [218] |
| Cobalt oxide  | Screen printing     | 1–12     | 54.9–60.3           | < 1 min       | [220] |
| MnO₂/GPLE     | Electrodeposition   | 1.5–12.5 | 57.051              | 20 s in acidic medium and 60 s in alkaline medium | [226] |

### Footnotes

1. The dissolution of these phases [60].
2. The change was much faster than in cold water (shown in Fig. 7g).
3. The Pechini method allows the sensor fabrication at low temperature and it has future potential advantages in flexible RuO₂ based pH sensor fabrication.
4. Zhuiykov [159] developed a new sensing material based on Bi₂Ru₂O₇₋ₓRuO₂ for online monitoring of pH of water.
5. The measurement (Fig. 7g) shows the response/recovery rates for the freshly prepared and the sensor used for 12 months. When the sensor was stored in water, the sensor response/ recovery rate is influenced by the biofouling effect.
6. The measurement (Fig. 7g) shows the response/recovery rates for the freshly prepared and the sensor used for 12 months. When the sensor was stored in water, the sensor response/ recovery rate is influenced by the biofouling effect.
It was found that ions: Cl$^-$, NO$_3^-$, SO$_4^{2-}$, F$^-$, I$^-$, Ca$^{2+}$, K$^+$ have little influence on the sensing performance [2,22,82]. However, RuO$_2$ sensitive electrode made of a commercial paste shows susceptibility to interferences caused by anions and slow response in basic solution. Labrador et al. [82] developed a theoretical model to determine the response of thick film pH sensor based on the commercial RuO$_2$ paste. The experimental analysis of the interferences of common anions obtained by the fixed interference method is presented in Fig. 7h. The model explains the redox potential behavior of complex electrodes containing a mixture of MO$_x$ involved in redox processes and enables evaluation of interfering influence of some anions. The sensing performance and methods of fabrication of a few RuO$_2$ based sensors are also listed in Table 3.

One of the major reported applications of RuO$_2$ based pH sensors has been water quality monitoring. Martinez-Manez et al. [22] developed a multi-sensor by thick film technology (screen printing) for monitoring water quality parameters in making use of the RuO$_2$ sensing layer for determining the pH of water. Other water quality parameters such as DO (dissolved oxygen), temperature, turbidity and conductivity were also determined. This multi-sensor applied for online monitoring of water pollution seems to solve the drawbacks of traditional systems employed for this purpose [22]. For online monitoring of water pollution, Zhuiykov [2] and Atkinson et al. [20] developed integrated multi-sensors with pH sensors based on RuO$_2$ sensing electrodes (shown in Fig. 7f). Furthermore, RuO$_2$ based pH sensor was also utilized for measuring pH of several beverages. Koncki and Mascini [160] demonstrated a disposable pH sensor prepared by screen printing technique and studied its potential application for pH analyzing of food drinks, like Fanta, wine, milk, cola and orange juice. The obtained results were comparable with those determined using a conventional glass pH electrode. We had developed a new LTCC based pH sensor aimed at miniaturization, cost reduction and integration of the sensor part with passive components in a single substrate for wireless application [23,101]. These potentiometric pH sensors with the SEs based on commercial RuO$_2$ paste as well as the prepared RuO$_2$-Ta$_2$O$_5$ and RuO$_2$-Ta$_2$O$_5$-glass compositions fabricated by LTCC technology exhibited excellent sensing performance. The developed LTCC based pH sensors were also successfully tested in wireless monitoring system [23,101]. Liao and Chou [58] used RuO$_2$ thin film as a hydrogen sensing layer in an ISFET type sensor. This pH sensor was also applied for measuring pH of a few fluid foods, like cola, yogurt, water and milk [10,42,154]. For this application, RuO$_2$ sensitive electrode printed on alumina substrate and a pseudo reference electrode (RE consisting of a thin film of RuO$_2$ electrode modified with a polyvinylbutyral (PVB)-SiO$_2$ layer) embedded in 3D printed housing (shown in Fig. 7j) were used [42]. The measured pH values are in good agreement with those obtained using the conventional glass pH electrode. The fabricated 3D printed device exhibited its potential application for the online water quality monitoring and glass free pH sensor applications.

6.2. Iridium oxide (IrO$_2$) based pH sensor

Among different MO$_x$ for pH sensors, IrO$_2$ has shown excellent stability over a wide pH range at high temperature up to 250 °C, at high pressure, and in aggressive environment, as well as a fast response even in non-aqueous solutions [161,162]. IrO$_2$ crystallizes in the rutile structure [163] similar to RuO$_2$ but exhibits lower catalytic activity than RuO$_2$. Besides its pH sensing application, IrO$_2$ is also well known as an anode material for oxygen and chlorine evolution and as an electrochromic material [164,165]. The characteristics of IrO$_2$ sensors are very sensitive to the film structure and composition, which depend on the fabrication procedure (a few works are mentioned in Table 3). Considering these aspects, Katsube et al. [161] explored a pH sensor based on metal-MO$_x$ configuration, an IrO$_2$ film deposited by sputtering method on various substrates including titanium and tantalum. The sensing electrode was stable in aqueous solutions at temperatures up to 200 °C. The films sputtered on stainless steel and tantalum substrates show a Nernstian response with the slope factor of 59 mV/pH. It was found that due to different structure of the film the electrochemical reactions occurring at the IrO$_2$ film prepared by sputtering and anodization methods are different.

The sol-gel method can provide a simpler and economically feasible approach for low temperature fabrication of iridium oxide film. Nishio et al. [166] adapted dip coating process for preparation of IrO$_2$ film. For the fabrication of SE, iridium chloride was used as a starting material in solution preparation and the deposited film was heat treated at 300 °C. Based on Nishio et al. [166] work, Huang et al. [40] developed a flexible IrO$_2$ pH sensor on a polymeric substrate as shown in Fig. 8a. The sensor shows a sensitivity of 51.1 mV/pH in the pH range of 1.5–12 at 25 °C [40]. This flexible sensor exhibits excellent sensitivity, response time, stability, reversibility, repeatability and selectivity [40]. Based on this work, Nguyen et al. [167] fabricated pH sensors array, consisting of 16 individual sensors (SE based on IrO$_2$ and RE based on Ag/AgCl) on a single polyamide flexible substrate by sol-gel method. For mapping pH value across the surface, a thick layer of PDMS polymer with 4 × 4 punched-out wells (with a diameter of 5 mm) was placed on top of the surface of the sensors and all the sensors were conformal on the outer surface of a plastic tube (3.5 cm in radius) for measurement. This experimental setup ensured that the test solutions stayed on the top of individual sensors without mixing with each other. The developed sensors in arrays exhibit sensitivity close to Nernstian responses in the range of 57.0–63.4 mV/pH [167].

The Ir salts are more expensive than Ru salts, for reducing the cost of IrO$_2$ SE, Da Silva et al. [85] prepared a binary oxide IrO$_2$-TiO$_2$ and utilized polymeric precursor method for the sensor fabrication. They developed SE on titanium substrate based on the composition of IrO$_2$-TiO$_2$ with (100–0), (70–30), (30–70) and (20–80) mol%. The electrode based on IrO$_2$-TiO$_2$ (30–70) mol% in the range of pH 1–13 shows excellent sensitivity, fast response and good reproducibility [85]. Wang et al. [55] have reported a new method based on chemical oxidation called ‘carbonate melt oxidation’ for developing iridium pH electrode with long-term stability. Iridium metal wire was coated with a uniform iridium oxide film by oxidation of the wire in a carbonate melt. In a wide pH range, this pH sensor exhibits excellent sensitivity and long lifetime. Moreover, it is suited for continuous pH measurement without the need of frequent calibration [55]. IrO$_2$ based micro-electrochemical transistor for pH sensing fabricated by anodic electrodeposition was reported by Pasztor et al. [168]. The sensor shows the sensitivity of 65 mV/pH, higher than the theoretical value in the pH range 1.8–12, and the response time of 40 s. A pH sensor fabricated by anodic electrodeposition of IrO$_2$ film was also developed by Marzouk et al. [56] for physiological application such as measurement of extracellular myocardial acidosis during acute ischemia. Such
method has potential applications in developing pH sensors on flexible substrates for wearable applications.

Kinlen et al. [169] developed a new approach for fabrication of pH sensor which is based on a polymer Nafion-coated IrO2 electrode and a polymer modified Ag/AgCl RE. The Nafion layer on IrO2 surface after annealing becomes permselective to cations. Maintaining the electrode sensitivity to pH, it eliminates or attenuates many of anionic interferences. The authors reported that the polymer based RE is helpful to trap the Cl\(^-\) ion in the polymer layer by encapsulating it with a Na\(^+\) outer layer. After annealing, the Na\(^+\) membrane effectively blocks Cl\(^-\) diffusion to the test solution and maintains a constant Cl\(^-\) activity on the AgCl surface, and thus a constant electrode potential. Hence, by applying this method one of the drawbacks of a MOx pH sensor, related to response to redox species in the solution which leads to errors in pH measurement, can be avoided [169].

IrO2 based sensors received promising applications in many fields including biomedical ones. Kreider [162] fabricated by sputtering IrO2 pH sensor suitable for high temperature, high pressure application in the nuclear repositories system. The sensor shows a linear response of approximately 53–58 mV/pH at room temperature in a wide range of solution conditions. For a biomedical application, Prats-Alfonso et al. [57] reported a urea biosensor based on anodic electrodeposited iridium oxide film pH electrodes modified with urease coated magnetic particles. They observed the area of the electrode does not have significant differences in sensitivity (slope shown in Fig. 8b). For environmental application, recently Yang et al. [138] proposed fully portable pH sensor based on IrO2-rGO sensitive layer. The device consists of an integrated miniaturized programmed paper-fluidic electrochemical pH platform (schematic representation is shown in Fig. 8c) integrated with portable pH meter powered by batteries to make digital pH test strips for in-field measurements. The major advantage of pH platform is that it combines advantages of both pH strips and pH meters for water quality monitoring. The IrO2 – rGO SE exhibited a slightly super Nernstian response (61.7 mV/pH) in the range of pH 2–12 with response time less than 250 s and hysteresis width 13 mV in different cycle shown in Fig. 8d [138].

Monitoring the stability of pH of organs such as the heart is an important biomarker in health monitoring. However, the traditional electrochemical pH sensor using glass electrode is not able to be utilized in such application because it is rigid, hard, shows bulky behavior and provides only single measurement channel. The advanced flexible pH sensor overcomes some of these drawbacks of the glass electrode. However, the limitation of stretchability or possibility to conform to complex three-dimensional surfaces of
flexible sensor prevent applications areas of the heart in ways that do not constrain natural motions. Chung et al. [170] developed IrO2 based stretchable arrays of pH sensors. It was found that in the developed solution interconnected arrays of IrO2 pH sensors encapsulated in thin, low-modulus elastomers can yield conformal monitoring system capable of noninvasive measurements on conformal laminations onto the time-dynamic epicardial surfaces of the beating heart. The sensor shows a super-Nernstian sensitivity with excellent repeatability (69.9 ± 2.2 mV/pH). [K+] and [Mg2+] are the two cations that are present in the extracellular space during ischemia. It was observed that the range of potential variation with influence of these ions was less than 3.5 mV, which corresponds to \( \approx 0.05 \) pH [170]. The influence of measuring media temperature is a very important factor in pH sensing mechanism. In this study the developed sensor shows a linear dependence of \(-1.63 \pm 0.02\) mV/C for temperatures between 20 and 60 °C [170]. In addition to this for wearable application, to attach a conformal surface on the body, highly flexible sensors are required, especially for sweat monitoring applications. For this, the sensor cloth will be a great advantage and has recently been achieved by the electrodeposition of IrO2 film on conductive cloth [171]. The developed textile on cloth which shows sensitivity of 47.54 mV/pH for sweat monitoring. Authors observed that the sweat pH measurement in human skin using the fabricated sensor shows a relative error of 4% when compared with a standard pH measuring method.

6.3. Tantalum oxide (Ta2O5) based pH sensors

The materials based on Pt-group metals are very expensive, so the research interest has been directed towards the development of pH sensors using cheaper materials. Among these materials, Ta2O5 has received significant attention, in particular for the fabrication of pH-ISFETs due to its high sensitivity (59 mV/pH), low drift and lower surface deterioration due to oxidation [71,172]. Ta2O5 has found interesting applications as a proton conductor, catalyst, high dielectric constant gate insulator, optical coating material with high refractive index and low loss. For Ta2O5 pH-ISFET, diffusion and phenomena described by the site-binding model are known to be responsible for the sensing mechanism [71]. The crystalline structure of Ta2O5 film exhibits a significant influence on the sensing performance. So, heat treatment procedure of the sensing membrane has a substantial role in the sensitive layer fabrication [71]. The sensitivity of Ta2O5 oxide film depends on the amount of surface sites, so Ta/O ratio at the surface represents a critical parameter for the pH sensing mechanism. According to Kwon et al. [71], the Ta/O ratio in the sensing membrane is the most important parameter for the pH sensitivity. They suggested that with increasing O-sites at the surface, the sensitivity of the sensing membrane increases. A Ta2O5 film for pH ISFET sintered at 400 °C in O2-ambient shows excellent pH sensitivity (58–59 mV/pH) for a wide pH range (2–12) [71].

Recently, Chen et al. [70] developed Ta2O5 based electrolyte-ion sensitive membrane-oxide–semiconductor (EIOS) pH sensor for online pH monitoring in an acidic environment, as shown in Fig. 10a. When Ta2O5 is exposed to a solution, surface hydrolysis of Ta2O5 takes place leading to formation of tantalum hydroxyl groups (Ta-OH). This surface becomes charged either by donating or accepting protons during reaction with solutions containing H+/OH ions [70], as shown in Fig. 9a. The membrane and electrolyte interface lead to a network consisting of the double layer capacitance (Cdl), charge transfer resistance (Rct) and Warburg impedance (W), which is associated with the diffusion of ions from the electrolyte to the membrane. In this study, a two-electrode configuration (SE – Ta2O5 and RE- conventional Ag/AgCl) was used for EIS analysis of the sensor. The results of EIS studies of the sensor were as shown in Fig. 9b with equivalent circuit analysis (Fig. 9c). In the lower frequency range, the sensor shows Warburg impedance due to diffusion of ions from electrolyte to the membrane, as illustrated in Fig. 9b [70]. In our previous work we observed that the electrical properties of a thick film conductometric pH sensor based on Ta2O5 sensing layer are strongly dependent on the pH value in the low-frequency range. However, thick film potentiometric pH sensor with Ta2O5 sensing electrode exhibits a sub-Nernstian behavior. A combination of ionic exchange and electronic transfer may be the reason behind the pH sensing mechanism of Ta2O5 based pH sensor [69].

The breakable glass pH electrode has limitations in using for food processing applications. There is a great demand for “non-glass” pH sensors in food industry, biotechnology, water purification, etc., especially for online monitoring purpose. Schoning et al. [142] reported a pH sensor with the sensitive capacitive EIS structure (electrolyte-insulator-semiconductor) with Ta2O5 gate for in-line pH monitoring systems in food industry. The proposed sensor exhibits a sensitivity of 57 ± 1.5 mV/pH in the range of pH 2–12 [142]. The pH EIS based sensors with corrosion resistance against strong alkali solutions were developed by using Al2O3-Ta2O5 and Al2O3-ZrO2 sensitive materials. The sensor based on Al2O3-Ta2O5 showed higher pH sensitivity while Al2O3-ZrO2 layer was more effective in enhancing corrosion resistance against strong alkali solutions [173].

6.4. Tin oxide based pH sensors

Tin oxide is one of the most intensively studied semiconductor oxides for gas sensors [174,175], and little attention has been paid to its pH sensing application. Fog and Buck [52] reported that SnO2 based potentiometric pH sensor shows a sensitivity of 48.6 mV/pH. These authors mentioned that SnO2 in the doped form are not suitable for pH electrode fabrication, but functions mainly as a redox electrode. However, after this work only few studies were devoted to SnO2 as a pH sensitive material due to its applicability in a narrower dynamic range as compared with glass and other metal oxide based pH sensors [176]. The major studies concerning SnO2 pH sensors were carried out for ISFETs. Liao et al. reported SnO2 as a pH sensitive material prepared by using thermal evaporation or sputtering method for ISFET applications and also investigated sensing mechanism of pH ISFET [177]. They concluded that surface parameter \( \Delta Kp (pK_a - pK_b) \) is one of the dominant factors for pH response of ISFET [125,177]. Liao et al. [177] reported that SnO2 is a suitable pH sensitive layer regardless of deposition method. To confirm this claim, they developed different SnO2 based pH ISFETs, such as SnO2/SiO2 gate ISFET (SnO2 prepared by thermal evaporation method) which shows a sensitivity of 58 mV/pH, SnO2/Si3N4/
SiO$_2$ gate ISFET (SnO$_2$ deposited by r.f. reactive sputtering) with a sensitivity of 57 mV/pH and SnO$_2$/SiO$_2$ gate ISFET (SnO$_2$ developed by r.f. reactive sputtering) which exhibits a sensitivity of 55 mV/pH [177].

For the open gate FET based sensors such as the conventional ISFET, the influence of light can cause a considerable voltage shift. Chin et al. [67] found that SnO$_2$/Al discrete gate ISFET structure prepared by the standard CMOS IC processes exhibits a significant decrease in light sensitivity. The SnO$_2$/Al discrete structure of ISFET sensor consists of an open contact window and a MOSFET transistor. The window was covered by Al and plated with SnO$_2$ membrane for pH sensor [67]. Since thermal behavior has a strong influence on the properties of an ISFET sensor, it is necessary to determine effective methods to improve sensor stability. To realize this purpose, Chin et al. [178] fabricated a combined pH ISFET with SnO$_2$/Al multilayer electrodes and p-n diode temperature sensor. These authors presented detailed theoretical considerations and experimental behavior of both sensors. The fabricated pH sensor showed a sensitivity of 58 mV/pH in the pH range of 2–10 [67].

The method of preparation of the pH electrode influences the sensing performance. For example, Fog and Buck [52] observed that SnO$_2$/Al discrete gate ISFET structure prepared by the standard CMOS IC processes exhibits a significant decrease in light sensitivity. The SnO$_2$/Al discrete structure of ISFET sensor consists of an open contact window and a MOSFET transistor. The window was covered by Al and plated with SnO$_2$/Al membrane for pH sensor [67]. Since thermal behavior has a strong influence on the properties of an ISFET sensor, it is necessary to determine effective methods to improve sensor stability. To realize this purpose, Chin et al. [178] fabricated a combined pH ISFET with SnO$_2$/Al multilayer electrodes and p-n diode temperature sensor. These authors presented detailed theoretical considerations and experimental behavior of both sensors. The fabricated pH sensor showed a sensitivity of 58 mV/pH in the pH range of 2–10 [67].

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Hysteresis and drift are two phenomena which limit the accuracy of the pH ISFET sensors. There are few reports which proposed an improvement of the sensing characteristics by the control of these effects by sputtering and rapid thermal processing techniques.
Tsai et al. [145] prepared SnO2 thick film based pH ISFET by sputtering method. They investigated sensing behavior for the pH range 2–12 and found the pH sensitivity close to the theoretical Nernstian response and very low hysteresis effect. The recent studies of SnO2 based pH sensors have been concentrated on fabrication of EGFETs. In ISFET and EGFET structures either sapphire wafer or Si structure have been used as substrates. For reducing the cost and improving the sensing performance, Yin et al. fabricated by RF sputtering a pH sensor based on ion sensitive SnO2/ITO glass EGFET structure [133]. For the study of sensing performance, the authors used different sensing gate structures, such as SnO2/Al/micro slide glass, SnO2/Al/Corning glass, ITO glass, SnO2/ITO glass and ITO/micro slide glass. They observed that SnO2/ITO glass based sensing gate structure of EGFET has smaller drift and hysteresis effect and good sensitivity of 57 mV/pH [133]. Li et al. [68] demonstrated for the first time an EGFET with low-temperature hydrothermally synthesized SnO2 nanorods as the pH sensor. Batista et al. [181] reported the fabrication of a SnO2 based EGFET pH sensor by a low-cost sol-gel Pechini method.

The majority of SnO2 based pH sensors are fabricated using thin film technology. Only a few studies were devoted to thick film tin oxide-based pH sensors. Arshak et al. [111] investigated tin oxide sensing layers in a conductimetric IDE pH sensor. They found that both SnO and SnO2 operated well at low frequencies giving the best response to pH change in the range of 2–11. In their work, they noted that the device with both SnO and SnO2 electrodes cannot be utilized in reusable pH sensors [111]. Basing on EIS analysis of an IDE conductimetric pH sensor with thick film SnO2 electrode, we suggested that the sensing mechanism of the sensor can be attributed to the occurrence of charge transfer in the high frequency range and ionic conduction in the low frequency range [102].

There is growing interest of pH sensors in biomedical applications, especially for monitoring of bio substances, such as virus, protein and DNA. A FET based sensor is an interesting approach for this because of (i) gate electrode of FET is embedded in the device and not electrically connected to the test solution and (ii) does not require a reference electrode. Regarding materials for FET fabrication, more recently nanostructured semiconductor MOx materials with morphologies of nanoflowers, nanorattles, nanowires, nanotubes have received great interest due to large-surface to volume ratio of the nanomaterials, advantageous for optimizing the sensing performance. Cheng et al. [180] reported a SnO2 nanobelt based FET pH sensor (schematic representation is shown in Fig. 9d with an inset of SEM image of nanobelt) which shows sensitivity in the range of pH 5 to 8.5. Fig. 9e shows the real-time responses, the average channel conductance of a sensor in response to different pH values from 5.0 to 8.5 at ten different molar concentrations [180]. This change in conductance of the sensor with pH value of solution is due to the surface protonation/deprotonation on the SnO2 nanobelt. It was found the SnO2 nanorod (55.18 mV/pH) shows high sensitivity due to the high surface-to-volume ratio for the nanostructured material which provides larger surface sites and more effective sensing areas as compared to SnO2 thin film (48.04 mV/pH) [68].

6.5. Titanium oxide (TiO2) based pH sensors

Titanium oxide films are considered as good pH sensitive layers due to their high chemical stability. So far, different methods such as metal organic chemical vapour deposition (MOCVD) [62], sol-gel [61], anodization of Ti substrate [63], sputtering [144] etc. were used for the preparation of TiO2 pH SE. Recently, researchers proposed a new approach for the sensitivity of TiO2 nanotubes based pH sensor by irradiation with ultraviolet (UV) light/rays [63]. In this work, the fabrication of a pH sensor was carried out by electrochemical anodization of titanium substrate electrode leading to formation of TiO2 nanotube array. They found that the nanotube array significantly increases the electrode surface area and hence the modified Ti electrode with the amorphous TiO2 nanotube array film shows good sensitivity. The oxidation time of the electrode changes the properties of the nanotube array and consequently pH sensitivity. Later, TiO2 nanotube array film was irradiated with ultraviolet (UV) rays for improving electrode sensitivity [63]. After irradiation, the sensitivity was close to the theoretical Nernstian response. The UV irradiation improves the hydrophilic property of the electrode. They considered H+ ion diffusion as the response mechanism of the pH sensor. The sensor was successfully tested for measurements of the pH of some drinks [63]. Chen et al. [182] developed a conductimetric pH sensor based on TiO2/multiwall carbon nanotube (MWCNT)/cellulose hybrid nanocomposite. This sensor exhibited in the pH range of 1–12 two linear regions in the conductance dependence on pH. The large surface area of cellulose hybrid nanocomposite increases the number of adsorption sites for H3O+ ions and hence increases the pH sensitivity [182].

In an EGFET based pH sensor, the gate must be a high conductivity material to serve as pH sensitive layer. However, TiO2 possesses high sheet resistance because of its intrinsic property. So, for increasing the conductivity of TiO2 either doping with metallic ions or modification of TiO2 surface is necessary for the good sensing performance of TiO2 based EGFET pH sensor. Chou and Chen [144] increased the conductivity of TiO2 by doping with Ru metallic ions. They used co-sputtering method to develop Ru-doped TiO2 as a sensing electrode of EGFET [144]. The fabricated sensor which showed excellent pH sensing performance is mentioned in Table 3. For decreasing cost and temperature, easy processing and increasing the conductivity of gate electrode of EGFET, Huang et al. [183] developed using hydrothermal method an EGFET pH sensor based on TiO2 1D nanowire (NW) on a fluorine-doped tin oxide (FTO) substrate and compared the sensing performance with TiO2 film [183]. Due to the higher surface to volume ratio and higher conductivity of NW TiO2 this sensor exhibited better sensitivity (62 mV/pH; 0.064 mA/pH) than the sensitivity (50 mV/pH; 0.051 mA/pH) of TiO2 film based pH sensor [183]. The higher conductivity of TiO2 NWs is due to the lack of crystalline boundary along each NW and hence the presence of a larger number of oxygen related bonding sites for pH sensing. Moreover, the higher conductivity of TiO2 NWs allows for better gate control than for TiO2 film. It was observed that both devices exhibit a linear IGS–pH relationship in the range of pH 2–12 [183].

Shin [62] reported the pH sensing performance of TiO2 sensitive layer which was prepared by MOCVD method. In this work, investigated the pH sensing by capacitance-voltage measurement for electrolyte/insulator/silicon structures such as TiO2/SiO2/Si/Al and TiO2 films which were annealed in the temperature range of 700–1000 °C [62]. Shin [62] observed that as-deposited films
showed a sensitivity of 57.2 mV/pH. However, the best sensitivity and long term stability were found for the film annealed at 900 °C and the fabricated sensors had no light induced drift. Liao and Chou [61] have studied the pH sensing performance of thin film TiO2 coating prepared by sol-gel method, and the modified TiO2 film used for drug sensitive membrane. TiO2 film was immobilized by using phosphotungstic acid and polyvinyl chloride (PVC) to develop a procaine drug sensor, where TiO2 thin film was utilized as a drug sensitive membrane substrate. They observed that the sensitivity of TiO2 pH electrode was close to Nernstian response and the sensor exhibits low drift rate [61]. The fabricated procaine drug sensor exhibited a sensitivity of 55.03 mVpC−1 with a response time of 16 s [61]. We fabricated a thick film interdigitated TiO2 based conductimetric pH sensor along with portable ADS933, based impedance analyzer for characterization of the sensor in frequency range of 5–20 kHz [24,184]. The device is designed to enable the portable and autonomous operation for in-situ measurements as well as laboratory characterization of the sample. We observed that the electrical parameters of the TiO2 based sensor are strongly dependent on the pH of solution in the low frequency range and from RC equivalent circuit it was observed that charge transfer and ion exchange are the two major phenomena for the sensing performances of a TiO2 pH sensor.

6.6. Tungsten oxide (WO3) based pH sensors

The transition metal oxide WO3 is a promising hydrogen sensitive material used for measuring pH over a wide range. WO3 has been used for constructing micro-electrochemical pH sensors for different applications [185]. WO3 is a low cost and commonly available material with improved stability. The associated ease of morphological and structural control of the synthesized WO3 nanostructures, reversible change of conductivity, selectivity, high sensitivity and biocompatibility makes them suitable for biomedical applications [72]. In 1987 Natan et al. reported for the first time WO3 based microelectrochemical transistor pH sensor in which the sensor was operating either electrically or chemically by changing the gate voltage or the pH value of the solution [185]. Zhang and Xu [73] promoted utilization of CNTs in electrochemical sensors and for the first time reported a pH sensor based on MoOx-multiwalled CNTs (WO3/MWNT). Even though the fabricated sensor shows a sub-Nernstian response, it has excellent reproducibility, stability, anti-interference properties and potential for miniaturization [73]. They followed single phase interaction mechanism to explain the pH sensing mechanism of WO3 based pH sensors.

Chiang et al. [143] studied the influence of temperature, hysteresis, and drift on characteristics of a WO3 based pH ISFET sensor. They found that pH sensitivity increases with increasing temperature and the temperature coefficient is dependent on pH value. Hysteresis width depends on measurement loop time and path. The hysteresis increases with increasing loop time and for acidic solutions is smaller than for basic solutions. Furthermore, it was found that the drift rate increases exponentially with pH value [143]. Nowadays, there is demand for microelectrochemical pH sensors, especially miniaturized and reliable pH sensors for physiological applications, such as cell determination. Yamamoto et al. [74] fabricated a W/WO3 ultramicrosensor for monitoring of pH value of cultured endothelial cells and observation of the pH variation generated by normal, damaged and recovered endothelial cells. For wearable healthcare application, flexible WO3 based pH sensors have potential applications due to their biocompatibility. Recently, WO3 based pH sensors (area of 1 mm2) were fabricated on polyamide substrate (fabrication steps shown in Fig. 10a) which exhibit excellent sensitivity (−56.7 ± 1.3 mV/pH) in pH range 5–9, useful for monitoring physiological fluids [72]. The sensors show reversible performance (as presented in Fig. 10b) and a low reduction of 11.6% between the 1st and 3rd cycle. This decrease in sensitivity is due to the reactions at the electrode surface and charge sites saturation that occurs after long measurement [72].

6.7. Zinc oxide (ZnO) based pH sensors

The diverse beneficial properties of various nanostructured materials - nanorods, nanowires and nanotubes have attracted interest of researchers due to their potential application for the pH sensor fabrication [186–190]. Among these, ZnO-based nanostructured materials received great attention because of their electrochemical and biocompatible properties. The large surface area of ZnO nanostructures makes them more attractive for chemical, gas detection and biosensor applications [187–189]. Kang et al. [188] reported nanorods integrated with microchannel for pH measurement for investigating the change in conductance of the ZnO nanorods with variations of the pH in electrolyte solutions. In this work, ZnO nanorods exhibit a linear change in conductance being 8.5 nS/pH in the pH range 2–12 in the dark and 20 nS/pH when illuminated with UV light [188]. Batista and Mulato [191] used the sol-gel process (based on hydrolysis and polycondensation reactions) to develop ZnO EG-FET pH sensors. As compared to crystalline ZnO, amorphous ZnO (film deposited at 150 °C) based EG-FET shows a comparatively good sensitivity (38 mV/pH). The reason for this effect may be that pure and amorphous ZnO material would increase the number of surface sites (Ns from eq. (3)) leading to better sensing performance [191].

The various nanostructures of ZnO, such as nanorods, nanowires and nanotubes, have various influence on pH sensing performance. Fulati et al. [78] developed a new pH sensor based on ZnO nanotubes and compared its pH sensing performance with that of nanorod structures. They found that ZnO nanotubes provide sensitivity (45.9 mV/pH) two times greater than the sensitivity (28.4 mV/pH) of ZnO nanorods in the pH range 4–12. Fulati et al. [78] suggested that this difference in sensitivity occurs because ZnO nanotubes of low dimensionality have higher levels of surface and subsurface oxygen vacancies and provide large effective surface area with higher surface-to-volume ratio as compared to ZnO nanorods. The difference in surface charge distribution at two walls of the metal oxide-electrolyte interface for ZnO nanorods and nanotubes in the CaCl2 electrolyte is shown in Fig. 10c and d, respectively [78]. ZnO nanotubes and nanorods are more stable for pH close to 7 and dissolve much faster when pH is deviating from the neutral value. Therefore, such sensors are more useful for biological fluids [78]. A detailed investigation on the mechanism of pH-sensing using ZnO nanorods, with an emphasis on the nano-interface mechanism was described by Hilli and Magnus [148].
The nontoxicity and biocompatibility of ZnO received great attention for miniaturized sensors for biomedical application. Chiu et al. [192] reported that the dangling bonds and surface states density induced on the surface of ZnO thin-film and the sidewall surface of the ZnO nanorod array may cause the Fermi level pinning effect and due to this effect the sensing parameters could not be effectively changed with the pH value solution of EGFET based pH sensor. In order to suppress the influence of Fermi level pinning, authors employed photoelectrochemical method to passivate the ZnO thin-film and the sidewall surface of ZnO nanorod [192]. Similarly, for ZnO unpassivated film has sensitivity of 38.46 mV/pH and for passivated film the sensitivity is 42.37 mV/pH [192].

6.8. CuO based pH sensor

Among nanostructured p-type semiconductor materials, CuO received a prominent position for multi-sensing applications, such as glucose, pH and gas sensors [25,193–196]. In addition, CuO also found applications in photodetectors, solar cells, supercapacitors and batteries, due to its high surface to volume ratio which enhances the sensitivity, selectivity, catalytic activity and its unique electrical and electrochemical properties [197–203]. The possibility of promoting electron transfer at a low potential, ease of synthesis and preparation of different nanostructures, shapes and dimensions, and environmentally friendly nature are advantages of this material in electrochemical applications [204]. The electrochemical properties of CuO are strongly dependent on morphologies because of different specific surface areas. Numerous methods have recently been reported to synthesize various CuO nanostructures.
with different morphologies (1D, 2D and 3D) such as nanoparticles, nanotubes, nanoflowers nanoribbons, nanoleaves, nanorods, etc. by using various chemical and physical methods [196,202–207]. However, limited studies were carried out to investigate the pH sensing performance of these CuO nanomaterials. Zaman et al. [207] reported that CuO nanoflowers (NF) exhibited sub-Nernstian response of 28 mV/pH in the range of pH 2–11. We observed that the surface morphology influences (FESEM imags of CuO NF and CuO nanorectangles (NR) are shown in Fig. 10e and f) the charge transfer phenomena of the MOx–solution interface and hence the sensor performance, as confirmed by the EIS studies (Fig. 10g) [25]. The CuO nanoractangle based sensors have better stability with respect to CuO nanoflowers based sensor. It was observed that the CuO nanoractangle based sensor exhibits a sensitivity of 0.64 μF/pH in the range of pH 5–8.5 (shown in Fig. 10h). For wearable applications, the flexible CuO nanoractangle based pH sensor shows negligible interference to other ions and analytes, such as Na⁺, K⁺, glucose, and urea [25].

6.9. Yttria stabilized zirconia (YSZ) based pH sensors

In the past few decades, there has been more concentration on measuring the pH of aqueous solutions at high temperature and high pressure, especially in applications involving nuclear power, geothermal energy, fossil power, oil well drilling, scale deposition, crystal growth, corrosion and hydrometallurgy [208,209]. Initially, the major works in this area were focused on hydrogen concentration cells and palladium hydride electrodes. However, use of these pH measurement devices is limited to the systems that are stable against the reduction by hydrogen and these sensors cannot be used for monitoring of pH of the high temperature aqueous systems containing oxidizing species. Niedrach [210] developed a promising material, YSZ membrane sensor for high-temperature potentiometry. Mcdonald et al. [209] used YSZ based pH sensor which obeyed Nernstian behavior for measurements up to 300 °C. Seneviratne et al. [211] reported a flow-through electrochemical cell with a flow through yttria-stabilized zirconia sensor and a flow through external reference electrode which was used for the first time for measuring pH at 250 °C in process sulfate systems relevant to hydrometallurgical process of nickeliferous laterites [211]. YSZ sensors are often applied in geothermal situations, like the acidic gases emanating from a volcano, and for nuclear power devices, especially nuclear waste disposal sites.

6.10. CeO₂ based pH sensors

Betelu et al. [212] reported the fabrication of CeO₂ based screen printed pH SE and its application for continuous pH measurement of the pore water in the Callovo-Oxfordian formation (COx) during its evolution as a radioactive waste repository. Zr or Sm was substituted to CeO₂ for improving the sensitivity of the electrode. Potentiometric method was used for monitoring the pH of the pore water. The EIS studies of the SE showed that in the low frequency range the mass transport (diffusion-convection) occurs at the electrolyte/electrode interface. In the high frequency range, the response was attributed to the charge transfer phenomena [212]. These authors found that a Zr substituted CeO₂ sensitive electrode shows better sensitivity in the pH range of 5.5–13.5 at 25 °C than Sm substituted electrode and a single oxygen intercalation is responsible for the pH sensing mechanism of CeO₂ based sensor [212].

6.11. Lead oxide (PbO₂) based pH sensors

Lead Oxide is exploited in various electrochemical applications. The deficiency of oxygen or excess of lead in PbO₂ results in its characteristic metallic conductivity. In PbO₂ both the lead and the oxygen ions are involved in electrochemical reactions. Due to excellent electrochemical properties, lead oxide has been used for pH sensor fabrication. Eftekhari [213] reported the possibility of fabrication of two modified electrodes α-PbO₂ and β-PbO₂ on aluminum substrate electrode for pH measurements. The aluminum substrate electrode helps to improve the stability and growth of the electroactive film. These electrodes are also used for the measurement of pH during flow injection analysis and measurement of pH of some real samples, like soft drinks and fruit juices [213]. Razmi et al. [214] presented α-PbO₂ and β-PbO₂ on a carbon ceramic electrode for pH measurements. The electrochemical properties of the PbO₂ film were improved by using the carbon composite electrode. The fabricated sensors are very suitable for measuring the pH of natural samples. The PbO₂ sensing film coated on carbon ceramic electrode shows excellent response time, high selectivity, good stability and long term usage [214].

6.12. Lithium lanthanum titanate based pH sensor

Bohnke et al. [96] explored the use of high lithium conductive perovskite compound lithium lanthanum titanate (LLTO) as a pH sensor. The authors tried to investigate the mechanism of pH detection of LLTO based sensors by using impedance spectroscopic analysis [96]. The pH sensor based on LLTO found applications in the food industry [215]. Even though it does not follow the Nernstian response, it shows good sensitivity and response time. The authors followed two methods for the preparation of ion selective electrode and electrochemical cell, comprising membrane configuration with liquid or solid internal reference [216]. Vijayakumar et al. [217] prepared LLTO pH sensor by solid state reaction and sol-gel method. According to them, in the solid state reaction method small grain size of the powder is favorable for proper pH sensitivity and the sensitivity increases when the LLTO powder is ground before heat treatment. Moreover, compared to the solid state method, sol-gel reaction requires much less time for powder preparation and permits to obtain pure and high quality LLTO [217].
6.13. Other MOx based pH sensors

In addition to the materials described above there are some works concerning the fabrication of pH sensors by using other oxides: MnO2 [218,219], cobalt oxide [220,221], molybdenum bronzes [222], NiO [223], Ni3(PO4)2·8H2O nano/microflakes layer on nickel foam (NF) [224], CeTi3O7 film [225], manganese oxide nanoparticles electrodeposited on graphenized pencil lead electrode [226], indium tin oxide (ITO) [134], etc. We presented here only some important materials which are widely used for pH sensor fabrication.

7. Comparison of pH sensing performance of MOx sensors

This review demonstrated that the sensing performance of the MOx based pH sensors is influenced by many factors including fabrication process, and material properties. Form the investigation we observed that the major approaches reported in literature for the fabrication of MOx pH sensors are: screen printing, sputtering, sol-gel, carbonate melt oxidation, electrodeposition, chemical vapor deposition, and Pechini method, etc. The pH sensing performance of various MOx sensors is shown in Fig. 11, where a comparison of some selected features, applicability, cost and sensing performance of pH sensors with metal oxide electrodes are schematically illustrated. In Fig. 11a, some characteristic properties of thick film, thin film and glass electrode based pH sensors are compared. It was observed that in comparison with glass and thin film based pH sensors, the thick film based pH sensors have many advantages for future applications in terms of fabrication of multi-sensors on a single substrate, fabrication of compatible RE with easy fabrication, low cost of fabrication along with excellent sensing performance. The parameters of pH sensors fabricated by different methods are illustrated in Fig. 11b. The screen printing method offers many advantageous properties (described in Fig. 11b). The nanostructure of the material influences the response time of the sensor. Thin film based deposition method can enable tuning the nanostructure of the material and can lead to a faster response than for thick film based pH sensors. A comparison of the sensing performance and the cost of most widely used MOx based pH sensors are shown in Fig. 11c. The sensing performance of each material is strongly influenced by the method of fabrication and structure of the material. Comparison of the average sensitivities of various materials shows that RuO2 based sensors have very good sensing performance even though the cost of these materials is high.

Even though many remarkable advances have been reported in the MOx based pH sensors, many challenges remain for development of pH sensors, especially concerning different applications such as biomedical, food and water quality monitoring. The major
design and development efforts in the field are focused on flexible, wearable, portable, miniaturized sensors for online monitoring applications. Some of new advances in pH sensing technology based on metal oxides, full measurement systems and compatible REs are summarized in Fig. 12. These include a ZnO based self-powered flexible pH sensor [230], shown in Fig. 12a, self-powered pH sensor using energy autonomous system (shown in Fig. 12b) [3], RFID tag pH sensor based on CNT chemi-resistor for wireless application (shown in Fig. 12c) [89], a miniaturized pH sensor based on thin film of Ag/AgCl RE and IrO₂ SE packaged in an SD card (shown in Fig. 12d) [231], a flexible electrolyte-gated neuron transistor with amorphous oxide (IZO-Indium Zinc Oxide) channel layers for biochemical pH sensing applications (shown in Fig. 12e) [41], disposable Ag/AgCl RE prepared on paper substrate by screen printing [232] and flexible Ag/AgCl/KCl based RE fabricated by screen printing method (presented in Fig. 12f) [103].

To address the emerging challenges, one of the future directions will be using proper sensitive materials for electrochemical MOₓ pH sensors to make them suitable for applications such as food processing, environmental monitoring and biomedical applications, etc. Concerning materials and design of sensors the major challenges are toxicity of materials, cost, flexibility and bendability of materials, integration of SE and RE on single substrate for potentiometric sensors miniaturization. Among others, the cost-effective fabrication, choice of substrates, and easy integration of sensors are some of the important issues to be considered. The scope of some future and potential solutions as well as current challenges are described below. The major drawback in majority of metal oxide based sensors is their slow response in neutral and basic solutions. This need to be overcome because the major application field of sensors lies in the pH range of 5–10. One of the alternative method is to mix metal oxide with conductive material; in such case the conductive material will act as a path of ion transfer. The electrochemical double layer formation in conductive element (for example, graphite) and pseudocapacitance of MOₓ will collectively involve in the electrochemical reactions.

7.1. Water quality monitoring

As an alternative to traditional glass based pH sensors, RuO₂ based pH sensors received promising attention in water quality monitoring due to its high sensitivity and chemical stability for a long period. However, the higher cost and low sensitivity in basic solution hinders the use of RuO₂ in many practical applications. The issues related to RuO₂ based electrodes are being addressed with mixed oxides or doped oxides. Another option is SE based on ceramic materials [233,234] such as doped or undoped ZrO₂ [235]. However, there are not many studies focused on ceramic materials, for example, Pb-free perovskites for pH-SEs. An interesting
alternative is also application of LTCC technology for fabrication of pH sensors with sensitive SE based on ceramic materials. The major advantages of this technology are (i) using cheap and simple screen printing method for deposition of sensing and reference electrodes (ii) possibility of integration in a LTCC substrate passive components for wireless application, e.g. for online monitoring of water pollution, and (iii) advances in sensor miniaturization and reliability. For realization of this purpose, a challenging task is preparation of an Ag/AgCl RE compatible with LTCC substrate. In previous works [23], preparation of glass-KCl composition functioning as a salt bridge seemed to be a crucial obstacle in RE fabrication. It can be overcome by using the possibilities of different glass-KCl compositions which are compatible with LTCC substrate. Such sensors have a significant application potential for multi-sensors and water pollution monitoring systems and aquaculture [236–238].

7.2. Food quality monitoring

In the food processing plant, “non-glass” pH sensors have great importance to ensure the quality of food. For example, in the meat industry, it is difficult to insert glass electrodes inside the meat because of possible breaking of the glass. In such case, pH sensors on alumina substrate should be very useful. Sensitive materials based on nanostructured ZnO, Ta2O5 or SnO2 will be advantageous due to their biocompatibility and high sensitivity. These materials will also be suitable for fabrication of flexible pH sensors which can be disposable. For food quality monitoring sensors, during the fabrication and characterization of sensors it is necessary to consider the influence of the fatty acids or other proteins particles present in the food. Flexible pH sensor on a food package with embedded RFID tags and communication system can predict the quality of food for producers and consumers.

7.3. Wearable biosensors for medical application

The electrochemical biosensors provide a simple and attractive way for analyzing the biological samples (sweat, urine, tears) through direct measurement of electrochemical reactions [239]. The monitoring of pH value of skin is important to detect pathogenesis of skin diseases like irritant contact dermatitis, acne vulgaris, atopic dermatitis, etc. [240,241] The pH of skin is related to pH of sweat [242,243]. Moreover, the continuous monitoring of pH value of blood and brain tissue is very important for the patients who have suffered stroke and traumatic brain injury. In addition, one of the greatest achievements in potentiometric pH sensors is the fabrication of novel wearable pH sensors for real time monitoring of pH changes in a wound. Hence, the development of new sensing biocompatible materials and designs is of fundamental importance in flexible electrochemical sensors for healthy life. The flexible or wearable pH sensors have great importance for early stage determination of many chronic diseases. For example, the diabetic patient’s simultaneous changes in level of pH and glucose effect the body metabolism. Hence, for better performance and selectivity of the sensor, flexible multi-sensor patches, which consist of glucose, temperature and other dissolved ions monitoring electrodes on a single substrate, may be useful for sweat analysis [244,245]. Flexible RFID with electronics wireless communication will be advantageous for online monitoring sweat and we show this in our recent graphite based pH sensor [4]. Inkjet printing or screen printing method can be the right approach for electrode fabrication for such sensors. For long term applications, nanostructured or doped ZnO, SnO2 or TiO2 inks and pastes will be suitable for sensitive electrode fabrication. For on body monitoring, a sensor printed on clothes or tattoo may be useful wearable application. Flexible triboelectric nanogenerator [246] for power supply to the electronic part which can be integrated with the wearable sensor will be helpful for online monitoring.

Until now, few MOx have been used for the construction of the electrochemical flexible pH sensors. The major MOx materials reported for flexible, disposable and wearable sensors included IrO2 [40,247], RuO2 [160,248], ZnO [77], ITO [249], IZO [41] and WO3 [72]. Synthesis of new nanostructured materials and implementation of novel designs are necessary for the further development of electrochemical pH sensors. More works should be carried out for IGZO (Indium Gallium ZnO) and GTZO (Ga-Sn-ZnO) based sensitive materials for flexible pH sensor applications. IGZO [250] shows good pH sensing and very good performance for thin film transistor applications. Sol-gel method may be one of the best options for the preparation of low cost nanostructured sensitive materials for large area of flexible devices. The major problem of this method is the deposition of MOx on a flexible polymer or paper based substrate at low temperature. Self-energy generating combustion method of material preparation can overcome this issue [251]. It enables developing transparent conductive oxide based thin large-area, low-cost electronics for sensor arrays. The fabricated sensors can be integrated into textile, tattoo, skin, wrist watches, bandages, etc. Another interesting approach is the preparation of nanoparticle growth on the surface of a substrate for single molecule determination of biological samples. The morphologies based on nanotubes, and nanorectangles should be very interesting due to large surface area for detecting the particles. For transferring the nano morphological samples on the top of flexible substrate tactile printing or contact printing methods should be promising approaches. We recently reported a flexible capacitive sensor for energy autonomous application, prepared by transfer printing method [252] and nanostructures fabricated by contact printing method [253,254].

7.4. Extreme environment applications

For applications at high temperature, high pressure and in aggressive chemical environment (e.g. in nuclear respiratory systems), LTCC based pH sensors seem to be well fitted. Doped or undoped CeO2 and ZrO2 [255] based sensors are well fitted for high temperature applications. Preparation of new co-firable pastes based on these compounds for LTCC technology may be a good approach for a new pH sensor design. To overcome the issue of RE, differential electrode prepared on the same substrate by screen printing method [248] may be a good attempt for RE fabrication instead of Ag/AgCl RE. Moreover, instead of potentiometric pH sensors, IDE based conductimetric pH sensors can be a better alternative. However, the major practical limitation of IDE based pH
sensors is the strong influence of the solution conductivity and degradation of materials. This problem can be overcome by using high dielectric materials or perovskite-based composites as SEs and suitable dimensions of IDE, as well as by measurement of conductivity by a sensor integrated with the pH sensor. In high and low temperature application of the sensor, the sensitivity and standard potential values are changing with temperature [256]. Thus, for future online monitoring applications of pH sensors it is necessary to ensure integration of electronic parts and control the changes of potential with temperature to minimize its influence on sensing performance.

7.5. Energy autonomous sensors

Power requirement for operating the sensors for online monitoring is a critical challenge. The chemi-reistive, ISFET based sensors require an operating potential. Moreover, the electronic circuits for online data transfer and storage also require suitable power sources. The bulky battery has many disadvantages in such application, including heating, toxicity, life cycle, frequent charging, etc. To overcome these challenges, energy autonomous sensors combining integration of energy generator (for example solar cell) and storage (for example supercapacitor) with the sensors and electronic components will have tremendous application in online monitoring. In our previous work [3,118,257], we used flexible solar cell and supercapacitor as power pack for voltage source to sensors for wearable application and also for water quality monitoring by integrating with robotic fish [258,259]. Further improvement is needed for the wireless application. The energy is required to deliver power for the electronic circuits and for remote applications including those in extreme environmental conditions. New strategies are demanded in this field, similar to those used for other applications.

8. Conclusion

The increasing demand for reliable sensors for online monitoring focuses the pH sensors based research on fabrication of metal oxides MOx. Such sensors, including those fabricated using thin and thick film techniques, have been gaining significant importance in current electrochemical sensing technology. This paper presented an overview of the fabrication methods, measurement techniques and the sensing performances of widely used MOx based pH sensors. Major techniques employed to provide the information about the sensing mechanism of MOx based pH sensors were also described. With fast responses, wider pH sensing range, excellent sensitivity, easy integration with microelectronic components, wearable structural compatibility, biocompatibility, ability to integrate with clothes, paper, skin, etc., the MOx based pH sensors offer a number of advantages over glass based sensors. In the present review, the development perspectives for MOx based pH sensors were demonstrated including flexible devices for online or in vivo biomedical applications, food quality monitoring and environmental monitoring.

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