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Electrochemical Sensor for Environmental Monitoring System: A Review

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Abstract. Environmental monitoring has been one of the key to provide better safety measure in various sectors of life. The most famously featured technology in this area is the gas detecting system. It serves not only in an early-warning application, but also a continuous mean to provide background check of the atmospheric status of a specific area ranges. According to their principals, gas sensors can be separated into two categories; the conductive metal-oxides and the electrochemical-type, with the latter gaining more recognition over the last decade as the future standard component in any gas sensing apparatus. Within this article, the whole concept of an electrochemical gas sensor will be presented, including the basic science and the basic electronical engineering that runs the device. The main concern will be fallen onto a specific amperometric-type sensor as the most common electrochemical sensor in the market. Ultimately, since there are multiple parts that comprise a single electrochemical sensor, a special section will be written within this article to show the array of materials that are responsible to the sensing capabilities of the sensor, particularly in the area of sensitivity and selectivity of gases.

INTRODUCTION

In order to preserve the quality of breathable air and to create a warning system towards the population, a detection system is the first tool in authority disposal. Since the 1970s, the technology of gas detection system has been used widely, mainly in the industrial environment to detect gas leak or reaction failure. Nowadays, this technology can be applied across larger sectors, such as natural disaster mitigation and urban air monitoring. Gas detection system mainly consists of two main parts; the gas sensor that interact with the target gas, and the system that can translate the respond from the said interaction. The semiconducting metal-oxide gas sensor remains the most popular type of gas sensor to date. The built of the sensor consists of a ceramic tube with metal wire coiled around it to pass electricity as the primary source of heat[1]. A contact with gaseous substance on the heated surface of the tube yields an electrical response that is translated as signal. This makes a modification of the ceramic tube is significant to the sensitivity of the sensor. Studies showed that a change in the grain size, among other characteristics, was improving the sensitivity to the sensor linearly, both performed experimentally and numerically[2, 3].Considering such alteration to the microstructure of the material is not an unpopular approach, the potential of improvement in this area is quite promising.

However, the improvement effort of such sensor highly depends on the experimental methods. The more distinction between the concentration and the type of the targeted gas, the more specific materials requirement will be. This is not excluding the fact that reliable measurement is often difficult to obtain in harsher environment, or even in predictable environment with faster dynamic of observed variables[4]. With the need of a more reliable sensor sustainability and lower energy consumption, the trend in gas sensor has been shifting towards the electrochemical sensor-type[5]. Without the need of extra heating, the electrochemical sensor can be utilised in a long range of temperatures, spanning from -30 to 1600 ºC[6]. This is a tremendous upside towards building a sensor that is able to

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function in multiple facets of scientific and industrial fields. The sensor mechanism also allows the sensor to gain information in unruly places, mainly in the application of biological sensors[7]. The electrochemical sensor can be built differently, allowing the users greater flexibility in finding the right sensor for the right application. The two main types of electrochemical sensor based on the working principles are the potentiometric and amperometric types. The potentiometric type is usually involving solid electrolyte as the primary ionic conductor. The electrolyte conducts the ion of the measured targets, e.g. an oxygen-ion conductor for oxygen sensor. This type of sensor is not very commonly found in the market nowadays and is usually trusted to detect gases in high temperature condition, such as exhaust gas from automobile combustion[8]. The amperometric gas sensor is a current dominant force in the market due to the robustness of the sensor in different temperature, pressure, and chemical condition. Some claimed that it also reacts better in different concentration of dissolved ions and gases[9].

This article will review the basic principle of an amperometric electrochemical gas sensor and dismantle the component of the sensor from the material perspective.

THE PRINCIPLE OF ELECTROCHEMICAL SENSOR

A low-power electrochemical sensor device is usually able to detect gases at the parts-per-million (ppm) level. A newly-improved material can improve the sensor sensitivity, selectivity, and stability, or finds balance between these three criteria to detect a specific type of gas. The speed of detection is also a part of the concern, especially when dealing with utterly harmful gases. In order to develop a better gas sensor, the electrochemical setup of the sensor must be firstly understood.

The most common model of an amperometric, electrochemical gas sensor incorporates three electrodes as the main hub for ionic transports. These electrodes are separated by hydrophilic membranes known as wetting filters. The membranes are hydrophilic so that they can transport the electrolyte between the adjacent electrodes, enabling ions to move from and into them (Figure1)[10]. As any three electrodes system, it consists of the working, reference, and counter electrode to perform under the reduction-oxidation(redox) principle[11].

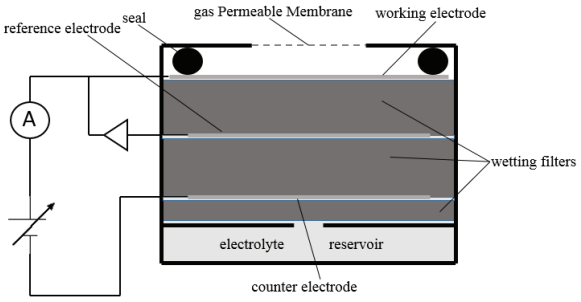

FIGURE 1. Design of a commercially, well-built, amperometric electrochemical gas sensor[10]

The working electrode is where reduction or oxidation happens, depending on how the system interacts with the observed gas species. For every reaction on the surface of the working electrode, it will draw a response from the balancing pole, the counter electrode. As the system comes on, the counter electrode will try to balance the change ofpotential as a result of reaction between the detected gases and the working electrode. This balancing current is dynamically monitored as the main reading of an amperometric electrochemical sensor. In order for the system to sustain, the potential on the working electrode must be inherently fixed with the use of reference electrode[12]. Owing to these balancing mechanisms, the three-electrode design can maintain the sensor sensitivity and linearity for the better part of its lifetime. A gas permeable membrane usually acts as a gateway for gases to enter the system. This hydrophobic membrane will separate the water from the gases well as regulates the amount of gas that is allowed to reach the surface of the working electrode while preventing any leakage of the liquid from inside the sensor (Figure 2).

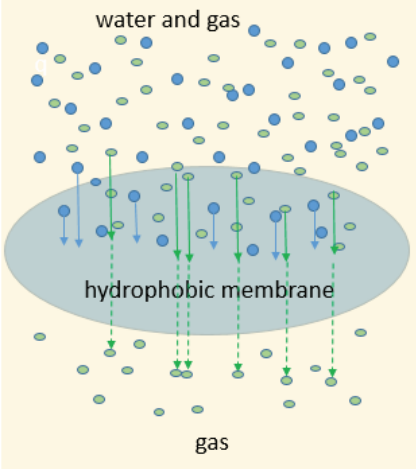

FIGURE 2. Hydrophobic membrane preventing the leakage of electrolyte from the sensor[12]

The arrangement is usually perfected for better performance or to accommodate a specific configuration in gas detection. Modern gas sensor, like shown in Figure 1, adopts the design of a clark-type gas sensor that was originally intended for medical devices that is closely attached to the idea of gas detection, such as a monitoring device for in-vivo oxygen level measurement[13].Despite being the most commercially successful type of electrochemical gas sensor, special attention must be given during application design, especially in the area of electronic circuitry and connection. This is due to the complexity of the design and the small current generated by the sensor.

Electromagnetic interference, cross-current, the stability of the catalytic electrodes, and leakage from interfering gases can be a continuing issues in a long run despite the reliability status this type of sensor is renowned for[14].

THE MATERIALS OF ELECTROCHEMICAL SENSOR

As major components for an amperometric electrochemical sensor have been described above, it is important to understand the quality of a specific component based on its material derived from. Many of the potential improvement on the reliability of the sensor are heavily directed to the modification of the materials involved. To simplify things, the elaboration will be discussed separately for each component.

Gas Permeable Membrane

The design of a membrane follows the mechanism of how the gas will reach the surface of the electrodes. A full retarding effect of gas transport uses a highly-clad thin membrane with very low porosity. While a faster circulation requires a capillary-type membrane with high porosity. Polymer-based material is usually the primary choice for membrane, i.e. teflon. Another attachment to the sensor is installed if necessary, like a so-called scrubber filter to prevent more unwanted gases entering the sensor. The most commonly used material for this type of filter is activated charcoal, proven to be able to filter almost any chemicals bar carbon monoxide and hydrogen gases.

Electrodes

The main concern in any electrochemical sensor research is to improve the function and productivity of the main working electrode. The result can always be validated immediately in the same sensor system. This makes such improvement is more approachable and quantifiable in any applicable condition. Typically, electrodes are made from noble metals, such as gold and platinum, but in the current state of technology, many even utilised polymers-based and ceramics-based electrodes. For instance, the most common CO sensor uses platinum black fixed to a porous PTFE membrane as electrodes[15]. The modification is not limited to the way sensor material was selected. It goes further to introduce a surface modification, usually by coating method, multiple techniques and materials.

It was reported that composite-like materials exhibit the best result, and in some cases a more stable arrangement when combined with solid electrolyte. A case of carbon-platinum (C/Pt) thin film nanocomposite was presented as a catalytic surface deposit on a PTFE template using DC magnetron sputtering device[16, 17]. The result showed an improvement in detecting CO and H_2S compared to commercial sensor, Nemoto NE4. Plenty of improvement were declared in many studies with the same approach, a modification in the material and deposition technique on the surface of the electrodes: WO_3 powder painted or screen-printed on an Au-deposited YSZ pellet[18]; CuO-ZnO nanocomposite (prepared with impregnation technique) painted on Pt/YSZ disc[19]; A composite of sodium-based ceramics with addition of Zr-based ceramics as the main body of a solid cast electrode[20]; and many more.

The increasing attention towards rare-earth material has also been kind to the development of better sensor, given that many studies have been done to prove the uniqueness of its electrical properties. In one study, both active electrodes and inactive electrodes as parts of the system were all prepared from rare-earth metal oxides; $Ce_{1-x}Zr_xO_2$, and $La_{0.5}Sr_{0.5}CoO_3$ - $La_{0.5}Sr_{0.5}FeO_3$ - $La_{0.5}Sr_{0.5}NiO_3$ - $La_{0.5}Sr_{0.5}Co_{0.8}Ni_{0.2}O_3$ - $La_{0.5}Sr_{0.5}Mn_{0.8}Ni_{0.2}O$, respectively[21].

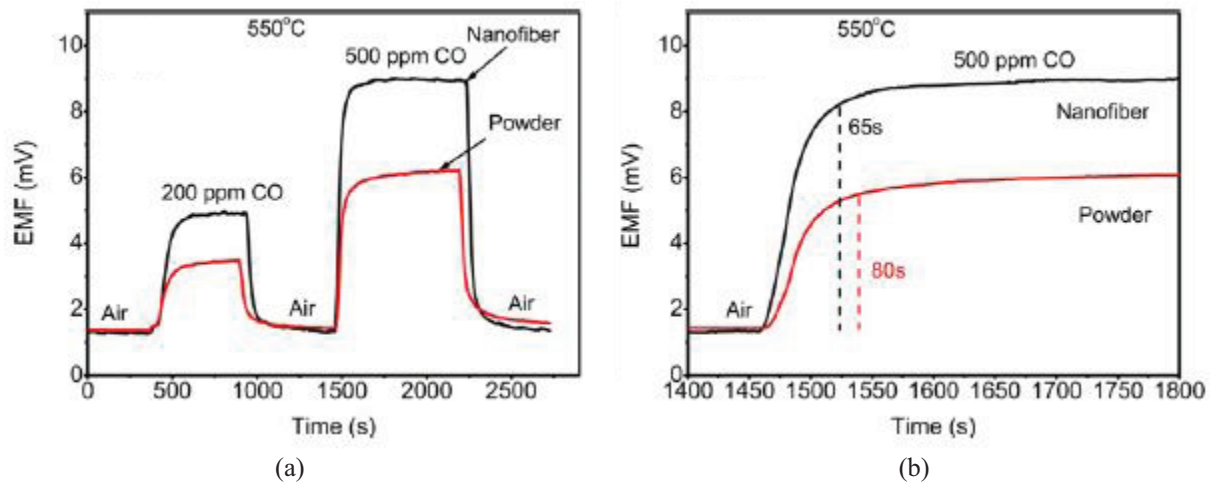

FIGURE 3. The improvement shown in transient response and estimated response time in CO concentration at 550º C for LSM modified sensor [22]

Some of the preparation for the deposition of rare-earth metal oxide can even be called unconventional. A lanthanum-strontium-manganite (La0:8Sr0:2MnO3, LSM) layer was successfully deposited on the surface of Pt electrode by using nanofiber electrospinning[22]. Figure 3 shows the improvement results of transient response and estimated response time in CO concentration at 550º C for LSM nanofiber sensor and the powder sensor. The LSM nanofiber sensor produced a faster response correspond to CO gas concentration. The process was also involving a sintering at 600º C to burn off any leftover inorganic material. The incorporation of advanced engineered materials, like the multi walled carbon nanotubes (MWCNT), on the surface of electrode is also a possibility. Successful coating on Pt with MWCNT-IIP (ion-imprinted polymer) was performed to functionalize the sensor into being able to detect Cd (II) ion and extract the said ion perpetually[23]. The coating was done via ion imprinting with the help of 0.5 % nafion to help solubilize and immobilize the layer simultaneously during the process.

Electrolytes

As ions transporting medium, electrolytes are expected to facilitate the ionic movement better as to support sustainable sensor performance. Current sensor development encourages the use of solid electrolyte instead of the liquid ones (sulfonic acid, sulfuric acid, buffer solutions, etc) for faster sensing capability and minimum maintenance. The most common material in these state-of-the-art sensor is yttria-stabilized zirconia (YSZ) plate, like in the referred articles above[19, 22]. Some of the researches in this field were using the same base material as electrolyte, electrode, and the adhesive that glues the two together as to maximize the potential of the newly developed material and to create a more stable electrical junction within the system. For example, doped lanthanum gallate electrolyte $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.1}Ni_{0.1}O_3$(LSGMN) was synthesized and used after sintering as an electrolyte disc that connects Pt/lanthanum-based electrodes on its surface via screen printing [21].

Polymer-based electrolytes are also becoming more popular as they offer, among other traits, excellent long-term stability. In the previous section, one of the most popular proton-conducting polymer (PCP) known as nafion was proven to be able to perform well in MWCNT-based electrochemical sensor[23]. In one study, a Pt/carbon black (CB) was mixed into a suspension of anion-conducting polymer (ACP), moulded and dried at 70º C for 3 h to obtain an electrolyte plate[24]. This plate was then layered on top of an ACP membrane to form a functioning electrochemical sensor. Electrochemical testing showed consistent reading that increased semi-linearly to the increase of CO_2 concentration.

CONCLUSION

Electrochemical sensors are both the trending product across sensor market worldwide, as well as the state-of-the-art technology with a bright prospect in the future. There are still plenty of improvements to be made as the quality of the material used in the sensor keeps improving. Engineered materials are the key to enhance the sensor sensing capability in a commonly marketed sensor, as well as increasing the sensitivity of ion selection for a specially-purposed sensor.

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REFERENCES

1. G. F. Fine, L. M. Cavanagh, A. Afonja, and R. Binions, *Sensors* ***10***, pp. 5469-5502 (2010).
2. C. Wang, L. Yin, L. Zhang, D. Xiang, and R. Gao, *Sensors* ***10***, pp. 2088-2106 (2010).
3. A. Rothschild and Y. Komem, *Journal of Applied Physics* ***95***, pp. 6374-6380 (2004).
4. P. Pasierb and M. Rekas, *Journal of Solid State Electrochemistry* ***13***, pp. 3-25 (2009)..
5. G. Jasinski, A. Strzelczyk, and P. Koscinski, *IOP Conference Series: Materials Science and Engineering* , p. 012034 (2016).
6. U. Guth, W. Vonau, and J. Zosel, *Measurement Science and Technology* ***20***, p. 042002 (2009).
7. V. M. Mirsky, *Ultrathin electrochemical chemo-and biosensors: technology and performance* ***2***: Springer Science & Business Media (2013).
8. E. Bakker and M. Telting-Diaz, *Analytical chemistry* ***76***, pp. 3285-3298 (2004).
9. Z. Cao, W. J. Buttner, and J. R. Stetter, *Electroanalysis* ***4***, pp. 253-266 (1992).
10. M. I. Mead, O. Popoola, G. Stewart, P. Landshoff, M. Calleja, M. Hayes, *et al.*, *Atmospheric Environment* ***70***, pp. 186-203, 2013.
11. V. V. Kharton, *Solid State Electrochemistry I.* (2009). Available: https://onlinelibrary.wiley.com/doi/abs/10.1002/9783527627868.fmatter
12. J. Chou, "Electrochemical Sensors," in *Hazardous gas monitors: a practical guide to selection, operation and applications*, ed: McGraw-Hill Professional Publishing, (2000).
13. L. Xiong and R. G. Compton, *Int. J. Electrochem. Sci* ***9***, pp. 7152-7181 (2014).
14. J. W. Fergus, *Sensors and Actuators B: Chemical* ***121***, pp. 652-663 (2007).
15. P. R. Warburton, M. P. Pagano, R. Hoover, M. Logman, K. Crytzer, and Y. J. Warburton, *Analytical chemistry* ***70***, pp. 998-1006, 1998.
16. E. Medvedeva and A. Baranov, *IOP Conference Series: Materials Science and Engineering*, p. 012052 (2018).
17. E. Medvedeva, A. Baranov, and A. Somov, *Sensors and Actuators B: Chemical* ***236***, pp. 858-864 (2016).
18. A. Dutta, N. Kaabbuathong, M. L. Grilli, E. Di Bartolomeo, and E. Traversa, *Journal of The Electrochemical Society* ***150***, pp. H33-H37 (2003).
19. N. Wu, M. Zhao, J.-G. Zheng, C. Jiang, B. Myers, S. Li, *et al. Nanotechnology,* ***16***, p. 2878 (2005).
20. Y. Sadaoka, Y. Sakai, and T. Manabe, *Sensors and Actuators B: Chemical* ***14***, pp. 532-535 (1993).

21. R. Sharan, M. Roy, A. Tyagi, and A. Dutta, *Sensors and Actuators B: Chemical* ***258***, pp. 454-460 (2018).
22. M. Zhi, A. Koneru, F. Yang, A. Manivannan, J. Li, and N. Wu, *Nanotechnology* ***23***, p. 305501 (2012).
23. A. Aravind and B. Mathew, *Journal of Analytical Science and Technology* ***9***, p. 22, (2018).
24. T. Hyodo, C. Ishibashi, K. Matsuo, K. Kaneyasu, H. Yanagi, and Y. Shimizu, *Electrochimica Acta* ***82***, pp. 19-25 (2012).