Transactions on Materials, Biotechnology and Life Sciences
ISSN: 2960-1932, eISSN: 2960-2319 | Volume 4
NSCBM 2024

Optimization of Electrochemical Sensors and Their Application in CO_2 Detection

Hongyi Zhang *

Queen Mary University of London Engineering School, Northwestern Polytechnical University,
Xi’an, China

* Corresponding Author Email: 553795769@mail.nwpu.edu.cn

Abstract. In response to the increasing global greenhouse gas content, electrochemical sensors with the advantages of existing main detection methods have the problem of being very sensitive to temperature, and long-term exposure to greenhouse gases will seriously affect the service life. From the aspects of sensitivity, selectivity, internal structure and working principle, this research points out the research progress of existing electrochemical sensors for detecting carbon dioxide (CO_2), which consist of ionic liquid base, solid polymer electrolyte, room temperature fluorinated anionic liquid and boric acid stable tungsten oxide solid electrolyte. It is also discussed that by optimizing the internal structure of the sensor and improving the composition of the sensor, the detection range and the applicable environment of the electrochemical sensor can be expanded, so as to reduce its sensitivity to temperature and finally achieve the result of prolonging its service life. On the basis of the research, the influence of different structures on the function of electrochemical sensor is discussed, the advantages of electrochemical sensor for CO_2 detection are analyzed, and the future detection of carbon dioxide by electrochemical sensor is prospected.

Keywords: electrochemical sensors; carbon dioxide; detection.

1. Introduction

The global average temperature continues to rise, triggering a series of extreme climate events, which have a profound impact on human life and the ecological environment of the earth. A El Nino warm current in the Northern Hemisphere spring of 2023, which expanded rapidly in the summer, is likely to further exacerbate the high temperatures in 2024. After peaking, the current usually has the greatest impact on global temperatures. At the same time, sea level temperatures and sea level rise reach record highs, and Antarctic Sea ice reach new lows. The Earth is experiencing a devastating climate collapse in real time. Observed concentrations of the three major greenhouse gases-carbon dioxide (CO_2), methane and nitrous oxide-reached record levels in 2022, marking a sobering milestone in the global climate crisis. As the world grapples with the impacts of climate change, it serves as a stark reminder of the urgent need for action.

Global warming has become a climate issue that governments at all levels and civil groups in the world focus on, and greenhouse gas emission reduction is an indispensable part of the solution to the issue, and research and development of accurate, rapid and dynamic detection of greenhouse gases applicable to different space and time scales is the basis and premise of environmental climate research. Currently, a myriad of greenhouse gas monitoring technologies exists both domestically and internationally. These technologies are essential in our fight against climate change and the detrimental effects of greenhouse gas emissions. Monitoring their emissions is crucial for understanding their impact and devising effective strategies to mitigate them [1]. While the electrochemical sensor is unique in the field of monitoring greenhouse gases because of its good measurement repeatability and accuracy, especially good selectivity for specific gases (such as CO_2).

Electrochemical sensors have the following advantages. First, it is able to detect gases with a certain selectivity, depending on the sensor type, target gas, and concentration. Second, it has a linear output, low power consumption and good resolution. Third, the electrochemical sensor has good repeatability and accuracy. After calibration to a known concentration, the sensor will provide repeatable, accurate readings of the target gas. Fourth, it is not easily polluted by other gases. The life of the sensor is not shortened by the presence of other gases in the environment. Finally, electrochemical sensors are more economical than other detection technologies. Electrochemical sensors are a cost-effective option [2]. The above advantages make the electrochemical sensors shine in the field of greenhouse gas monitoring, but it has to be mentioned that the electrochemical sensors are very sensitive to temperature and requires a very demanding use environment. And if prolonged exposure to greenhouse gases will seriously affect the service life.

Therefore, this research focuses on the application of electrochemical sensors for CO_2 detection and optimizes several problems existing in the electrochemical sensors. The details include the following aspects. Firstly, the sensitivity and selectivity of the sensor can be improved by optimizing the structural design and material selection of the sensor. The use of advanced nanomaterials or catalysts can enhance the sensor's response to the target gas and reduce interference signals. Secondly, improving the internal structure and working principle of the sensor can work stably under wider temperature and humidity conditions, and enhance the reliability of the sensor in different environments.

2. Application of electrochemical sensors for detection of CO_2

It is known that the measured current between the working electrode and the reverse electrode of the electrochemical sensor is proportional to the detected target concentration. According to the electrochemical transduction method used, electrochemical sensors are divided into potential sensors, voltamere/ampere sensors and conductance sensors.

Electrolytes are divided into liquid electrolytes and solid electrolytes. The liquid electrolyte is divided into water electrolyte and ionic liquid electrolyte. Water electrolyte is cheap and easy to use, but the volatility of the water electrolyte and the wide potential window limit the use of this sensor. When a water electrolyte is applied to a gas sensor, the pores of the sensor are filled, slowing the diffusion of the gas to the electrode, resulting in weak sensitivity. Therefore, research and development efforts focus on solid electrolytes or ionic liquids.

The room temperature liquid salt structure in the ionic liquid bypasses the extreme environment during the oxidation of methane analytes and has strong heat resistance and good ionic conductivity. At the same time, the boiling point is higher, less volatile, less harmful. However, there are some problems in the manufacturing process, which mainly focus on the leakage of liquid and the space occupied by liquid filling pores, which limits the diffusion channel of gas molecules and leads to slow diffusion of gas.

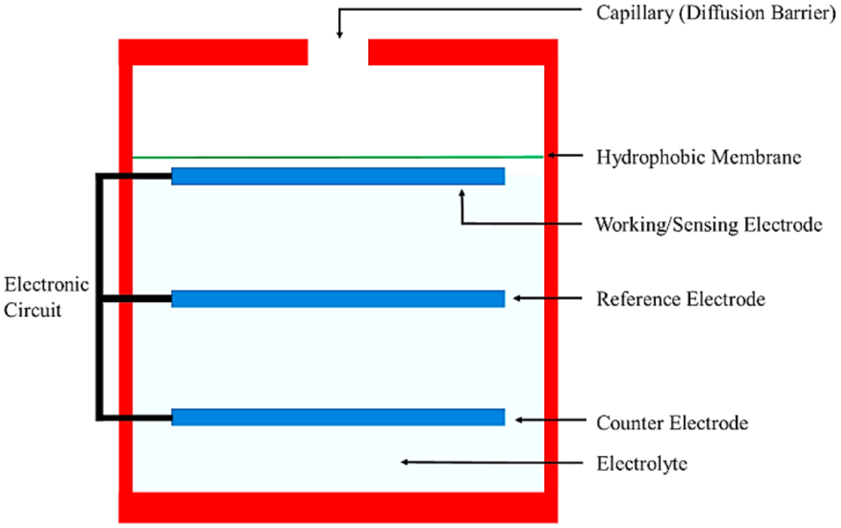

Fig. 1 Illustration of room temperature ampere-type electrochemical sensor [3].

Solid electrolyte sensors are generally composed of metal oxides, inorganic salts and doped polymers as solid electrolytes. Most sensors can only work at high temperatures where oxidation reactions occur and cannot be adapted to most use environments.

A hybrid potential sensor with minimal interference to NO, NO_2 and CO_2 in solid electrolytes was developed. As shown in Fig. 1, a room temperature ampere-type electrochemical sensor is proposed, which distributes the electrocatalyst on a carrier with high surface area to form a porous electrolyte and realize the room temperature electrooxidation of methane [3].

2.1. Different types of electrochemical sensors

2.1.1. Design of room temperature ionic liquid structures for fluorinated anions

There are three main types of CO_2 detector, the most common is the use of non-dispersive infrared spectral analysis form, can detect 0 ppm to 2000 ppm of different concentrations of CO_2. The disadvantage is that its photon source requires higher temperature sensitivity and consequent high voltage. The other is the use of electrolytic solution, due to the occurrence of irreversible reactions will affect the performance and narrow temperature range will affect the use of the environment. Therefore, the development of the next generation of CO_2 sensors needs to explore a new material.

Room temperature ionic liquid salts (RTILs) can withstand high temperatures of up to 300 °C without decomposition, with a wide electrochemical window and high capacitive response. When RTILs apply a potential, the electrode surface forms a shielding effect of anions or cations, and when exposed to different concentrations of CO_2, the overall impedance response of RTILs will rise with the increase of CO_2 concentration.

By using a gold electrode sensor with interleaving electrodes (IDEs), changes in the behavior of RTILs at the electrode interface when exposed to different concentrations of carbon dioxide were observed. The introduction of different concentrations of CO_2 validates the sensitivity detection of CO_2 by EMIM[BF4] and EMIM[FAP], which causes changes in capacitance. EMIM[BF4] capacitors are considered to be smaller sized anions, which have the ability to produce a denser filling EDL than EMIM[FAP]. This allows the CO_2 to interact more closely with the anions on the EDL. Because EMIM[BF4] capacitors have smaller anions and a denser EDL filling capacity, they can adsorb CO_2 molecules to the electrode surface more efficiently to improve the efficiency of CO_2 capture.

Although both materials have a high CO_2 absorption capacity, the ionic liquid EMIM[BF4] releases CO_2 more easily and quickly returns to baseline capacitance compared to EMIM[FAP]. This finding shows that EMIM[BF4] has the potential to be an ideal material for pure ionic liquid sensor type CO_2 sensors. The advantages of both materials are their liquid properties, high sensitivity to CO_2, and strong response to applied voltage. This means we can develop wearable devices with small electrode geometrics with the help of cutting-edge additive manufacturing techniques [4].

2.1.2. Ionic liquids in electrochemical sensors

The development of room temperature ionic liquids (RTILs) in stable electrochemical CO_2 sensors has been effectively applied. Two RTILs, gold and carbon paste electrodes, were designed on a printed circuit board with four different CO_2 concentrations. The effect of another RTILs on the initial repeatability of the gold electrode at two CO_2 concentrations was investigated. Through the organic combination of electrochemical impedance spectroscopy and time-current method, the initial CO_2 response behavior of these RTILs can be compared. This analysis helps to determine a robust combination of RTIL/electrode ambient CO_2 sensors.

RTILs generally refer to organic salts with melting points below 100 °C. An advantage of RTILs is that when they are deposited on the substrate (gold and carbon), they counteract any potential differences applied to the substrate surface and help ensure a smooth flow of electrons as they travel through the substrate. This Helmholtz-like electrochemical bilayer (EDL) allows large capacitance values to be measured at the interface using different electrochemical spectroscopy techniques, resulting in a large signal-to-noise ratio, which in turn allows the potential of RTILs as CO_2 sensors to be evaluated. By utilizing different electrochemical methods, it can further study and understand the performance of RTILs when detecting different CO_2 concentrations.

Electrochemical impedance spectroscopy (EIS) is a technique for studying changes in EDL, which can observe the response of EDL on a long time and small scale. The RTILs of two different anionic groups were analyzed. These RTILs are composed of 1-ethyl-3-methylimidazole tetrafluoroborate (EMIM[BF4]) and 1-ethyl-3-methylimidazole bis (trifluoromethyl sulfonyl) amide (EMIM[TF2N]). The cross electrode (ides) of a gold printed circuit board (PCB) provides a temperature-stable and chemically stable environment to observe the reaction. The effect of EMIM[TF2N] charge behavior on the gold electrode is realized by diffusion through the change of CO_2 concentration in RTIL. Of the two RTILs tested, EMIM[TF2N] also had a lower standard deviation in the test run. This means that the sensitivity of EDL to CO_2 concentration is consistent. When the resistance decreases linearly, and the capacitance increases linearly. In addition, the performance of EMIM[TF2N] is still in the research stage, and EMIM[TF2N] as a new CO_2 sensing medium needs to be further explored [5].

2.1.3. Miniaturized electrochemical sensors for ionic liquid for continuous monitoring

Electrochemical impedance technology has been widely used in many fields because of its advantages of non-invasive, low power consumption and low cost. An innovative single-frequency electrochemical impedance sensing (SF-EIS) method is available for real-time continuous CO_2 monitoring at low temperatures. This method enables real-time monitoring of CO_2 over a wide temperature range of -15 to 40 ℃. A miniaturized planar electrochemical sensor was prepared by using a hydrophobic 1-butyl-1-methylpyridine bis (trifluoromethylsulfonyl) imide (IL) electrolyte and Pt as electrode materials. IL forms a thin, ordered, concentrated layer of ionic charges to improve the sensitivity and selectivity of the sensor. IL has excellent impedance sensing performance at low temperature. Efficient monitoring of CO_2 can be achieved in the temperature range -15 to 40 ℃ by measuring impedance changes at specific frequencies of the open circuit potential (OCP). This result is due to the unique low temperature characteristics of ILs and EIS transduction mechanism, which provides a new possibility for gas monitoring in low temperature environment. This SF-EIS based CO_2 monitoring method shows excellent performance at low temperatures. Its many advantages make it widely used in the fields of environmental protection, industry and medical treatment. In addition, the study also provides a new idea for the application of electrochemical impedance technology in other fields and is expected to promote the development of related technologies.

SF-EIS has obvious advantages over electrochemical voltammetry. It enables real-time, non-destructive chemical sensing based on measuring changes in interface impedance at the electrode-electrolyte interface under AC perturbations of several mV amplitudes at a constant frequency. This new technology has great potential for long-term and continuous sensing applications, as low amplitude AC voltages cause minimal interference to the sensing interface and do not result in interfacial REDOX reactions.

SF-EIS technology has many advantages, but its performance in practical applications still needs further research. In order to improve the analytical performance of the SF-EIS sensing technology, the researchers made a unique optimization of it. First, by reducing the amplitude of the AC voltage, the interference in the sensing process can be reduced and the sensitivity of the sensor can be improved. Second, the optimized SF-EIS sensor has a higher anti-interference ability, which makes it have better stability in complex environments. In practical applications, S-EIS technology has been successfully applied to in-situ monitoring of CO_2 emissions in frozen soil. The dynamic change of greenhouse gases in permafrost region has an important impact on global climate change, so it is of great scientific value and practical significance to realize real-time monitoring of their emissions [6].

2.2. Solid electrolyte in electrochemical sensors

2.2.1. Laser induced graphene injection

To achieve efficient and sensitive detection, a method combining LIG electrodes with polyvinylidene fluoride (PVDF)/diacetylimidoformate (EMImTFSI) based solid polymer electrolyte (SPE) is available. This combination forms a composite material with a mesoporous/microporous network that not only improves the sensitivity of the sensor, but also enhances its response speed. With this design, sensors can quickly identify and respond to leaks, enabling real-time monitoring and rapid control of greenhouse gases.

The sensor uses laser-induced graphene to create a solid-state electrochemical sensor. The laser induced graphene interdigital electrode was modified with palladium nanoparticles by a simple solvent exchange method. By inhaling the PVDF/IL solid polymer electrolyte into the porous graphene electrode to form a porous electrolyte network, the analytes can be transported quickly. Under operating conditions with a low battery voltage of 0.6 V, the sensor produces a linear current response to varying methane concentrations in the range of 1 to 50 ppm. The sensor has a sensitivity of up to 0.55 $\mu A/ppm/cm^2$, a response time of just 40 seconds, and an experimental detection limit of 9 ppm. Compared with the electrochemical methane sensor reported in the past, the sensitivity and detection limit of the sensor at room temperature are reduced by nearly 4 orders of magnitude, showing high detection accuracy [7].

2.2.2. Tungsten-stabilized bismuth oxide solid electrolyte and cyclic voltammetry measurement technique

In the current trend of environmental protection, the research and development and application of gas sensors are increasingly paid attention to. A solid-state potentiometer battery sensor based on cyclic voltammetry (C-V) measurement technology is available. The sensor is able to precisely define the I-V curve (voltammetry) of each gas, with high accuracy when detecting gas concentrations.

During the research of the sensor, a unique and repeatable CO_2 response was achieved by improving the solid electrolyte material and using tungsten-stabilized bismuth oxide (WBO) as a new electrolyte material. The experimental results show that the porosity of WBO electrolyte has a significant effect on the CO_2 response. In a certain porosity range, the response speed and sensitivity of the sensor increase first and then decrease with the increase of porosity. This is because proper porosity can improve the contact area between the electrolyte and the gas, thus improving the response performance of the sensor. However, too high porosity can lead to reduced electrolyte stability, which in turn affects the performance of the sensor. Therefore, it is necessary to optimize the porosity of the WBO electrolyte during the study to achieve the best response performance.

The typical response of a WBO sensor to CO_2 shows a unique CO_2-related current that increases with increasing concentration. In contrast to the response associated with O_2, CO_2-related peaks appear in opposite polarity with respect to the upper and lower electrodes. The CO_2 sensing mechanism of WBO-based battery is related to the W component of solid electrolyte. Since the W in a WBO battery is contained in a solid electrolyte, CO_2 must be able to physically penetrate into the solid electrolyte. On the W electrode, CO_2 is almost completely desorbed to CO and atomic oxygen.

It was also found that the CO_2 sensing ability of the WBO sensor seemed to be related to the doping of W in the bismuth oxide solid electrolyte. The W atom in the bismuth oxide solid electrolyte can affect the process of CO_2 adsorption and deionization by changing its bonding state, so as to adjust the CO_2 response of the WBO sensor. In addition, it is shown that the CO_2 response of the WBO sensor depends on the porosity of the electrolyte. The larger the porosity, the larger the contact area between the W atom in the electrolyte and CO_2, and the faster the rate of CO_2 adsorption and deionization, resulting in a higher CO_2 response of the WBO sensor.

In order to better understand the effect of bonding state of W in WBO on CO_2 adsorption catalysis, future research work will try to characterize W atom. By analyzing the bonding state of the W atom in the WBO, it is hoped to confirm the presence of metallic bonds, which are necessary to catalyze the conversion of CO_2 to CO and atomic oxygen [8].

3. Conclusion

From the above content, this research summarizes the existing research on electrochemical sensors for CO_2 detection, focusing on the composition of sensor structures, mainly ionic liquids and solid polymer electrolytes. It can be seen that voltammetry sensing and fluorinated anion structure of ionic liquids, laser induced graphene injection of solid polymer electrolytes, WBO solid electrolytes, and sensing detection by cyclic voltammetry already exist. At present, the main research direction of CO_2 detection is focused on ionic liquids. In the future, the composition of ionic liquids can be further optimized to improve the range of applications for detecting temperature and humidity. In order to improve the detection efficiency and application range, it is necessary to develop solid electrolyte sensors. In addition, future research on CO_2 sensors should tend to optimize circuit design and processing algorithms to improve the sensitivity of the response.

References

[1] Bassous N J, Rodriguez A C, Leal C I L, et al. Significance of Various Sensing Mechanisms for Detecting Local and Atmospheric Greenhouse Gases: A Review. Advanced Sensor Research, 2024, 3(2): 2300094.

[2] Stetter J R, Penrose W R, Yao S. Sensors, chemical sensors, electrochemical sensors, and ECS. Journal of The Electrochemical Society, 2003, 150(2): S11.

[3] Aldhafeeri T, Tran M K, Vrolyk R, et al. A review of methane gas detection sensors: Recent developments and future perspectives. Inventions, 2020, 5(3): 28.

[4] Graef E W, Jagannath B, Munje R, et al. Fluorinated anionic room temperature ionic liquid-based CO2 electrochemical sensing. IEEE Sensors Journal, 2018, 18(9): 3517-3523.

[5] Graef E W, Munje R D, Prasad S. A robust electrochemical CO2 sensor utilizing room temperature ionic liquids. IEEE Transactions on Nanotechnology, 2017, 16(5): 826-831.

[6] Sridhar A S, Chen X, Glossmann T, et al. Single-frequency impedance studies on an ionic liquid-based miniaturized electrochemical sensor toward continuous low-temperature CO2 monitoring. ACS sensors, 2023, 8(1): 197-206.

[7] Dosi M, Lau I, Zhuang Y, et al. Ultrasensitive electrochemical methane sensors based on solid polymer electrolyte-infused laser-induced graphene. ACS applied materials & interfaces, 2019, 11(6): 6166-6173.

[8] Shoemaker E L, Kim C U, Vogt M C. CO2 sensing mechanisms of an electrocatalytic sensor based on a tungsten-stabilized bismuth oxide solid electrolyte and cyclic voltammetry measurement techniques. Sensors and Actuators B: Chemical, 2005, 110(1): 89-100.