ISSN: 2664-9640

Research on solid electrolyte and its application in CO_2 sensor

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Abstract

This paper mainly introduces the classification of CO2 sensors, the classification of solid electrolyte sensors, the research status of solid electrolyte, the doping of garnet type solid electrolyte and the application of several types of solid electrolyte in CO2 sensors.

Keywords

CO_2 gas sensor; solid electrolyte; garnet solid electrolyte.

1. Introduction

With the rapid development of industry, agriculture and transportation, coal, oil and other fossil fuels are widely used, resulting in the increasing concentration of CO_2 in the atmosphere, thus aggravating the global "greenhouse effect". Therefore, the development of new CO_2 sensors is an urgent task, and the development of new solid electrolyte materials is also a top priority. Compared with traditional models, new CO_2 sensors need to be improved in sensitivity, selectivity, stability, water resistance, response and recovery time. At the same time, in view of the large-scale use of CO_2 sensors, they need to be optimized in production cost, energy consumption, volume and miniaturization.

2. Overview of CO_2 sensor

Sensor is a device that can convert the measured data into available signals according to certain rules, mainly composed of sensitive elements and conversion elements. Sensitive element refers to the part in which the sensor can directly feel the measured part. The conversion element refers to the part of the sensor that can convert the output of the sensitive element into the electrical signal part suitable for transmission and measurement.

According to the detection principle, CO_2 sensors are mainly divided into infrared type, heat conduction type and electrochemical type. See the literature for relevant reports[1-3].

The infrared CO_2 sensor is based on the principle that CO_2 changes the transmittance of infrared ray with a specific wavelength. It has the advantages of wide measurement range, high sensitivity and good stability, but it has the disadvantages of large volume, high price and high maintenance cost.

Heat conduction CO_2 sensor detects CO_2 by measuring the difference of gas heat conductivity between detection element and reference element. This kind of sensor is small in size, but its accuracy, stability and gas selectivity are not ideal.

Electrochemical CO_2 sensor is a kind of chemical sensor that converts the concentration (or partial pressure) of CO_2 into electrical signal through electrochemical reaction. It can realize continuous monitoring on site, and has the advantages of low price, compact structure and convenient carrying. It can be divided into current type, electric quantity type and potential type. Solid electrolyte CO_2 sensor belongs to potential CO_2 sensor. Except solid electrolyte CO_2 sensor, it has the disadvantage that it must be used in electrolyte. Moreover, the solid electrolyte electromotive force gas sensor has the characteristics of high sensitivity, good selectivity, easy and accurate signal measurement and processing, and high accuracy.

3. Classification of solid electrolyte sensors

According to the different types of interface between electrolyte and target gas, solid electrolyte EMF CO_2 sensors are further divided into three types, namely type I, type II and type III, as shown in Fig. 1[4-5]. In the type I gas sensor, the detected material is converted into the movable material in the electrolyte. For example, the oxygen sensor shown in Fig. 1a. The reaction takes place at the three-phase boundary (TPB), in which the solid electrolyte is yttria stabilized zirconia (YSZ), and the sensitive electrode material is porous platinum, which contacts with oxygen phase. In TPB, oxygen molecules are adsorbed on the Pt surface and converted into O^{2-} ions, which further diffuse into the electrolyte[6-7]. Because the type of ions conducted by the solid electrolyte used in the type I sensor is the same as the type of gas detected by the target. Due to the limitation of this condition, this type of sensor can't detect some gases, so it can't be a CO_2 sensor. The type II gas sensor detects the same immobile substance in the sample and electrolyte through the reaction between the sample and the second mobile ion. For example, Fig. 1b shows Gauthier's CO_2 sensor, which uses K_2CO_3 as solid electrolyte, where K^+ ions are mobile ions[8]. Once adsorbed on TPB, carbon dioxide molecules react with K^+ ions in the electrolyte to form fixed K_2CO_3, which establishes a new chemical potential on the sensitive electrode and changes the electromotive force of the battery. However, the number of chemically stable combinations of solid electrolyte and sensitive electrode materials is limited to other gases, which is the main disadvantage of the principle of type II gas sensor[9]. In order to overcome the shortcomings of type I and type II, in Fig. 1c, the solid electrolyte used in type III sensor is sodium ion conductor, referred to as NASICON. Due to the use of Au and Na_2CO_3 composite auxiliary electrode, Na_2CO_3 and CO_2 gas participate in the electrode reaction, thus avoiding the direct contact between solid electrolyte and CO_2 gas.

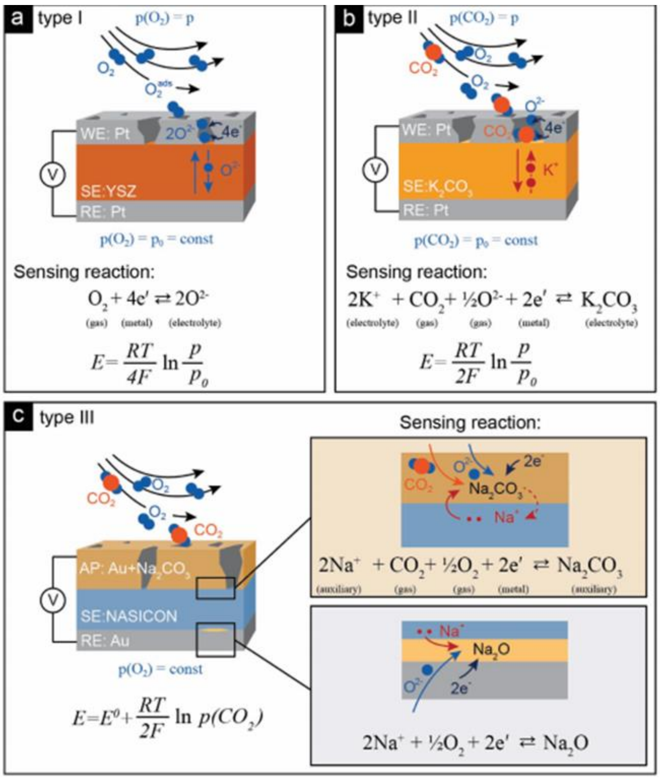

Figure. 1 three types of solid electrolyte electromotive force sensors

ISSN: 2664-9640

4. Research status of solid electrolyte

Solid electrolyte is a kind of solid material with ionic conductivity, also known as fast ionic conductor or super ionic conductor. At room temperature or low temperature, its conductivity is greater than 10^{-4}S/cm, and its activation energy is less than 0.5eV[10].

As shown in Fig. 2[11], according to different electrolyte materials, it can be divided into polymer solid electrolyte, oxide solid electrolyte and sulfide solid electrolyte.

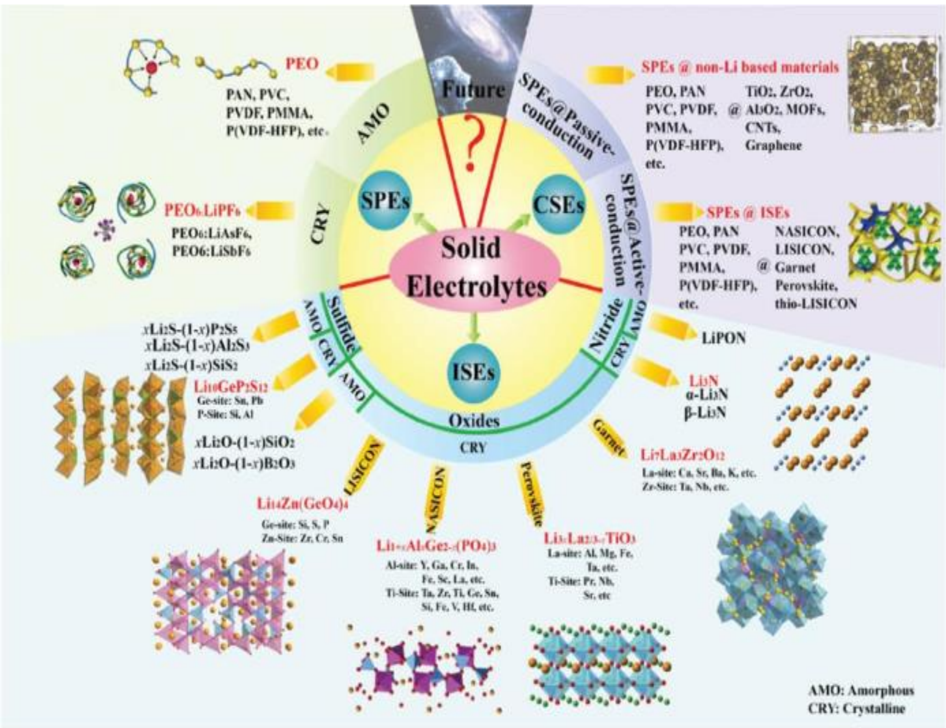

Figure. 2 classification of solid electrolytes

4.1. Polymer solid electrolyte

Polymer solid electrolyte (SPE) is composed of polymer matrix and lithium salt, which is a kind of electrolyte material formed by dispersing lithium salt in organic polymer. The main matrix of SPE is PEO, polysiloxane and aliphatic polycarbonate. PEO-lithium salt system is the representative of PEO based polymer solid electrolyte. In 1973, Wright *et al.*[12] reported for the first time that the complex formed by PEO material and alkali metal lithium salt has ionic conductivity, which pointed out the direction for the next research. The ionic conductivity of PEO is very low, only 10^{-7}S/cm-10^{-6}S/cm, because there are a lot of crystalline regions in PEO.

The advantage of polymer solid electrolyte is that it can meet the requirements of various sizes, shapes and thicknesses. The disadvantage is that the ionic conductivity of organic electrolytes is significantly lower than that of inorganic electrolytes. At low temperature, although it has high mechanical strength, the ionic conductivity is very low. When the temperature is higher than 60℃, the ionic conductivity increases, but the mechanical properties of PEO decrease.

4.2. Oxide solid electrolyte

The oxide solid electrolyte materials are mainly divided into LISICON type solid electrolyte, NASICON solid electrolyte, perovskite solid electrolyte and garnet solid electrolyte.

4.2.1 LISICON solid electrolyte

LISICON is lithium ion fast conductor. In 1978, Hong et al.[13] reported for the first time that LISICON material is Li14Zn(GeO4)4. The ionic conductivity of the material reaches 0.13S/cm at 300℃. In 2014, Santosh et al.[14] reported a material with LISICON structure, which can be regarded as a solid solution of Li_4SiO_4 and γ-Li_3PO_4. By replacing P^{5+} with Si^{4+}, more lithium ions are introduced into the structure gap, which greatly improves the ionic conductivity of the material. But LISICON solid electrolyte material has high ionic conductivity at high temperature, but low ionic conductivity at low temperature. If it is applied to CO_2 sensor, its low ionic conductivity at low temperature will reduce the sensitivity of the sensor and improve the response and recovery time. Therefore, its development and application are limited.

4.2.2 NASICON solid electrolyte

NASICON is sodium ion fast conductor. In 1976, Hong and Goodenough et al.[15-16] reported that the first NASICON material is Na1+xZr2SixP3-xO12, x=2.0. The material is a kind of sodium ion conductor. Morimoto *et al.*[17] prepared $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$(LATP) material in 2013 by substituting trivalent Al^{3+} for tetravalent Ti^{4+}. The experimental results show that the ionic conductivity of $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ reaches 3.0×10^{-3}S/cm at room temperature when x= 0.3.

Because of its excellent ionic conductivity, NASICON solid electrolyte has been widely used. However, NASICON solid electrolyte is very easy to react with CO_2 and H_2O in the air to generate Na_2CO_3, which affects the response, recovery time and stability of CO_2 sensor. Therefore, if it is to be used in CO_2 sensor, it is necessary to change the sensitive electrode and reference electrode materials, and change the sensor structure to improve the water resistance of NASICON based CO2 sensor.

4.2.3 Perovskite solid electrolyte

The perovskite structure was first reported by Takahashi and Iwahara[18-19], and the general formula is ABO_3(A=Ca, Sr, La; B=Al、Ti). $Li_{3x}La_{2/3-x}TiO_3$($0 < x < 0.16$) is a typical solid electrolyte with perovskite structure.

The conductivity of perovskite structure solid electrolyte is usually determined by the hole concentration in the crystal, the size of Li^+ transport bottleneck and the degree of crystal order. Therefore, the ionic conductivity can be improved by doping ions with larger atomic radius to increase the hole concentration. In order to improve the ionic conductivity of LLTO materials, Teranishi *et al.*[20] introduced Nd materials to modify LLTO materials, so that the ionic conductivity of LLTO materials increased to more than 10^{-4}S/cm.

4.2.4 Garnet type solid electrolyte

In 2005, Weppner *et al.*[21] reported the structure of $Li_5La_3M_2O_{12}$(M is Ta, Nb and other elements) solid electrolyte containing 5 Li. The ionic conductivity of the system is 10^{-6}S/cm. The ionic conductivity of the system is low. In 2007, Weppner *et al.*[22] reported the cubic phase $Li_7La_3Zr_2O_{12}$(LLZO) solid electrolyte material containing 7 Li, and the ionic conductivity of the material reached 10^{-4}S/cm. Due to the high ionic conductivity and high stability to lithium, the materials have attracted extensive attention and research upsurge.

However, garnet solid electrolyte was first prepared in 2005, but its ionic conductivity is low, so it can not be applied to CO_2 sensor. Until 2007, the solid electrolyte with ionic conductivity of 10^{-4}S/cm was prepared. Many subsequent scholars have carried out a variety of element doping or modification to improve the ionic conductivity of this new material, such as doping single or multiple elements such as Al, Ta and Nb. Therefore, the possibility of making garnet solid electrolyte based CO_2 sensor has emerged, but there is little research on it at present, which has great research prospects in changing solid electrolyte materials, water resistance and miniaturization.

4.3. Sulfide solid electrolyte

According to the classification of phase structure, sulfide solid electrolytes can be divided into three types: glassy, ceramic and glass-ceramic.

The research of glassy sulfide solid electrolytes is mainly focused on Li_2S-SiS_2 and Li_2S-P_2S_5. In 1988, Kennedy *et al.*[23] first reported that the ionic conductivity of doped Li_2S-SiS_2 was 10^{-4}S/cm.

Kanno *et al.*[24] found that $Li_{4-x}Ge_{1-x}P_xS_4$, a thio-LISICON solid electrolyte, has the highest ionic conductivity of 2.2×10^{-3}S/cm when x=0.75.

In 2002, Tatsumisago *et al.*[25] first reported the glass-ceramic Li_2S-P_2S_5 material with room temperature ionic conductivity of 10^{-3}S/cm.

The advantage of sulfide solid electrolyte is that among the listed solid electrolytes, it has the highest ionic conductivity, even higher than that of traditional liquid electrolytes, which is unmatched by other solid electrolytes. The disadvantage is that sulfide solid electrolyte is very sensitive to H_2O and O_2 in the air, and it is very easy to react with them, which will generate toxic gas H_2S, which increases the difficulty of manufacturing, raises the manufacturing cost, and is limited in large-scale application.

In addition to the solid electrolytes with various structures described above, there are also nitride solid electrolytes Li_3N and $Li_{2.88}PO_{3.73}N_{0.14}$, anti perovskite type Li_3OCl, composite metal hydride $LiBH_4$, iodide lithium ion conductor I_2-LiI(HPN)$_2$ and organic-inorganic composite solid electrolytes LLZO/PEO[26-31]. But these solid electrolytes also have some disadvantages, such as nitride solid electrolyte Li_3N, which is very unstable in the air. Organic-inorganic composite electrolyte is based on a large number of organic substances, which is poor in safety performance.

In summary, there are advantages and limitations in polymer, sulfide, LISICON, NASICON, perovskite and garnet solid electrolytes. However, in general, cubic $Li_7La_3Zr_2O_{12}$ has excellent stability and high ionic conductivity, which is the most promising oxide solid electrolyte at present.

5. Doping of garnet solid electrolyte and its application in CO_2 sensor

Although the garnet type solid electrolyte $Li_7La_3Zr_2O_{12}$ (LLZO) has high ionic conductivity and excellent stability compared with other types of solid electrolyte, the ionic conductivity is about 1 to 2 orders of magnitude lower than that of liquid electrolyte. Therefore, in order to improve the ionic conductivity, it is necessary to dope LLZO solid electrolyte.

5.1. Doping of LLZO solid electrolyte

5.1.1 Doping of Al

Al is the most common doping element in $Li_7La_3Zr_2O_{12}$, and the doping process is simple. The addition of Al can stabilize the cubic phase structure, improve the ionic conductivity and improve the electrochemical performance. Hu *et al.*[32] used $LiOH\cdot H_2O$, $La(OH)_3$, ZrO_2 and Al_2O_3 as raw materials, prepared Al-LLZO with cubic structure by traditional solid-state sintering at high temperature (800-950℃) according to the molar ratio of 7.7:3:2:(0.2-0.4). The results show that the target product has high ionic conductivity (2.11×10^{-4}S/cm, room temperature) when the Al doping amount is 0.3mol and the sintering temperature is 900℃. Xia *et al.*[33] prepared Al doped Al-LLZO with Li_2CO_3, La_2O_3, ZrO_2 and Al_2O_3 as raw materials by high-temperature solid-state method. The results show that the target product prepared by platinum crucible sintering has high ionic conductivity (4.48×10^{-4}S/cm, room temperature) and good chemical stability under the conditions of 0.25mol Al doping, 1200℃ sintering temperature and 24h sintering time.

5.1.2 Doping of other elements

Howard *et al.*[34] used La_2O_3, ZrO_2, Ga_2O_3 and Li_2CO_3 as raw materials, $Li_{5.5}Ga_{0.5}La_3Zr_2O_{12}$ with cubic structure was obtained by solid-state sintering and Ga doping in $Li_7La_3Zr_2O_{12}$, which showed good ionic conductivity. The results show that Ga doping is a method to improve the ionic conductivity of $Li_7La_3Zr_2O_{12}$. Dumon *et al.*[35] prepared Sr doped cubic LLZO by traditional solid-state synthesis method, and its ionic conductivity is 4.95×10^{-4}S/cm at room temperature. The room temperature conductivity of undoped LLZO is only 2.1×10^{-4}S/cm.

ISSN: 2664-9640

5.2. Application of solid electrolyte in CO_2 sensor

5.2.1 Garnet type solid electrolyte

Zhu *et al.*[36] used garnet type $Li_6BaLa_2Ta_2O_{12}$ as solid electrolyte, $Li_{0.36}WO_3$ as reference electrode, Li_2CO_3 and Au (3:2, wt%) composite electrode as working electrode to assemble the sensor. Preparation of solid electrolyte: La_2O_3, Li_2CO_3, $BaCO_3$ and Ta_2O_5 were sintered at 700℃ for 6h, then annealed at 900℃ for 24h and ball milled. By testing at 300-500℃, the ionic conductivity increases with the increase of temperature, and a number of tests have been carried out. The sensor shows a high sensitivity (73mV/decade), long-term stability, signal repeatability and fast response and recovery time. Struzik *et al.*[37] assembled CO_2 gas sensor with $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$ as solid electrolyte, Au as reference electrode and Au-Li_2CO_3 composite electrode as working electrode, and tested in the temperature range of 278-411℃ and the concentration range of 400-4000ppm CO_2. Compared with NASICON solid electrolyte, the response time can reach 1min at a lower temperature; And with the temperature increasing, the response time is gradually shortened; And in the long-term stability test, the performance is also very good.

5.2.2 NASICON type solid electrolyte

Kida *et al.*[38] used NASICON as solid electrolyte, Li_2CO_3 and $CaCO_3$ as auxiliary phases, so as to improve the sensitivity of the sensor to CO_2 at a lower temperature. However, the electrolyte was easy to react with H_2O, which maked the electrolyte unstable. Obata *et al.*[39] studied the sensing performance of potential CO_2 sensor based on NASICON under different humidity. Using $Na_{0.6}CoO_2$ as the reference electrode, the thermal stability and chemical stability of CO_2 sensor under humid conditions were greatly improved. Dang *et al.*[40] fabricated a planar CO_2 sensor with NASICON as solid electrolyte and NASICON, Pt and Li_2CO_3 as auxiliary electrodes. The temperature of the sensor was 300-500℃ and the concentration of CO_2 was 300-750ppm. The sensor can work normally at 400℃ and 500℃ under dry and humid conditions. At the same time, compared with the traditional sensor with Li_2CO_3 and $BaCO_3$ as auxiliary electrodes, the electromotive force value drift was small and the response time was very short. AoNo *et al.*[41] prepared $Na_3Zr_{2-(x/4)}Si_{2-x}P_{1+x}O_{12}$ (x=1.333) by sol-gel method, and CO_2 sensor was prepared using it as solid electrolyte, showing stable electromotive force and short response time.

5.2.3 LISICON type solid electrolyte

Satyanarayana *et al.*[42] studied the performance of CO_2 sensor with binary carbonate auxiliary phase based on Li_3PO_4 solid electrolyte. It was found that the influence of humidity on the sensor was significantly reduced when the auxiliary electrode material Li_2CO_3 was added with 10mol% $BaCO_3$ in the dry and 70% relative humidity gas environment with 500-5000ppm CO_2 concentration gradient at 500℃. Daddah *et al.*[43] studied the auxiliary electrode materials and sensitive electrode materials with LISICON as solid electrolyte, and improved the response and recovery time of the sensor by changing the sensitive electrode and auxiliary electrode materials. When the distance between the two electrodes is 0.25mm and the surface area of the auxiliary electrode is larger than that of the reference electrode, the response and recovery time of the sensor is the shortest. However, LISICON solid electrolyte has low ionic conductivity at low temperature.

6. Summary

There are many kinds of solid electrolytes, including polymer solid electrolytes, oxide solid electrolytes and sulfide solid electrolytes. However, the sulfide type, NASICON type and LISICON type solid electrolytes have obvious disadvantages, such as instability in air or low ionic conductivity, which are obviously inferior to the doped LLZO type solid electrolytes. Because of its high ionic conductivity and good stability, it is more suitable for the electrolytes of potential type CO_2 sensor. At the same time, other types of electrolytes have been widely

ISSN: 2664-9640

studied. However, the CO_2 sensor based on LLZO type and its doped garnet type solid electrolytes is less studied. The electrode structure and sensitivity, reference electrode materials and other aspects are improved, and the stability, response and recovery time, stability and stability are improved It has a great research prospect to improve the water resistance and sensitivity.

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