Solid Electrolyte Sensors for Emissions Monitoring

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There is an increasing need for chemical sensors that can work in extreme conditions. This means that the materials used to fabricate sensors must be stable at high temperature and/or in corrosive media. One approach for such an application is use of refractory metal oxides as sensor materials. If the oxides are ionic conductors, electrochemical (amperometric or potentiometric) sensors can be constructed. Solid electrolyte based chemical sensors for detection of pollutant gases have been investigated for many years and attracted wide attention. Potentiometric sensors based on solid ionic conductors constructed can exhibit sensory advantages that can be characterized by measurement of their sensitivity, selectivity, and detection range. This type of sensor is represented by the well-known stabilized zirconia (i.e., YSZ) based oxygen sensors, which have been widely used for air/fuel ratio control in the combustion engines. Over last 10 years, this type of sensor design has evolved to yield a new type of potentiometric sensors, called the surface-modified solid electrolyte gas sensors. Weppner gave a detailed classification of solid electrolyte gas sensors on the basis of the relations between the solid electrolyte and target gas,[1] which has helped promote new research on these so-called “Type III” gas sensors. One advantage of this approach to sensing gases is the development of detection methods at elevated temperatures. The significant characteristic of this type of sensor is that an auxiliary layer is coated on the surface of the solid electrolyte to provide sensitivity and selectivity for detection of the target gaseous species.[2] This approach allows the use of several conventional solid electrolytes, including YSZ, β-alumina, or NASICON[3,4] to construct sensors with specificity for several important gaseous agents. Particularly, this type of sensors shows promising potential for the measurement of several most important environmental gaseous pollutants, such as CO_2, CO, NO_x, SO_x, H_2, Cl_2, NH_3, which are usually difficult to detect by typical chemical sensors. In addition, the detection can be accomplished under harsh conditions. The design of the auxiliary materials is of critical importance to develop this type of sensors.

In the present work, NASICON, a fast Na^+-ionic conductor, with the composition of $Na_3Zr_2Si_2PO_{12}$, was prepared and used as a solid electrolyte. Several alkali metal salts were used as auxiliary phases to modify the surface of NASICON. The sensing performance, including sensitivity, response time, and stability, of the sensors will be presented and discussed. Fig. 1 illustrated a typical potential response to H_2 for a simple device with the structure of H_2, Pt/NASICON/Ag, AgCl. The sensing electrode was treated by diluted HCl solution, resulted in a partial ion exchange of Na^+ for H^+ ion on the surface of the NASICON. The sensor showed a reproducible EMF response to H_2 concentration changes. Modification of the sensing electrode of the sensor with a $NaNO_3$ layer allows the sensing of NO_x gases as shown in Fig. 2. Application at higher temperatures is possible with NASICON. In addition, exploration of new materials for sensitivity and for stabilization of the solid reference electrode will improve responses in field conditions.

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References

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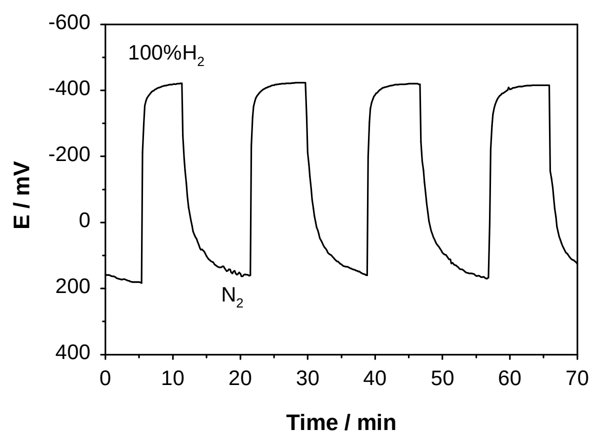

Fig. 1. Hydrogen response transient at 50ºC for the device of Pt/NASICON/Ag/AgCl. The sensing electrode was treated with diluted HCl solution.

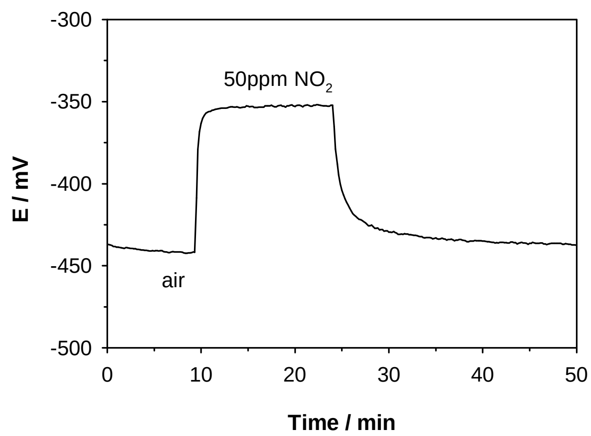

Fig. 2. Potential response curve to 50 ppm NO_2 at 195ºC for the device of Pt, NO_2, $NaNO_3$/NASICON/Au, air.