Tips for Selecting Polymeric Ethanol-sensing Materials: Detection Mechanisms and Sensing Materials

K. M. E. Stewart and A. Penlidis

(IPR Symposium (May 2015), Department of Chemical Engineering, University of Waterloo, Waterloo N2L 3G1 Canada)

Driving under the influence of alcohol (ethanol) is a major problem and results in numerous casualties and deaths each year (Solomon et al., 2012). Therefore, reliable monitoring of blood alcohol levels is needed. Currently, breathalyzers, which measure ethanol in the breath, are used; however, their frequency of use (typically sporadic spot checks) is limited. Also, interlock ignition systems are cumbersome and a distraction to the driver. The goal is to create a transdermal ethanol sensor that is less distracting to the driver and autolocks a vehicle’s ignition when ethanol is detected from the driver.

This goal results in a set of operating specifications that restrict the type of sensing materials used in such a sensor. For example, transdermal ethanol sensors must be very sensitive to ethanol and very selective due to the amount of other volatile organic compounds (VOCs) that are also emitted from the skin. Additionally, for an in-vehicle sensor, a polymeric sensing material must have a high glass transition temperature, since the internal temperature of a vehicle can range between -40°C and 60°C (Null, 2003). These constraints will aid in selecting appropriate sensing materials for ethanol and the target application.

When choosing polymeric sensing materials, it is important to look at how their functional groups and side chains will interact with the target analyte (in this case, ethanol). Determining the mechanisms by which the target analyte is likely to interact with a sensing material will help narrow down potential sensing materials for ethanol. For example, ethanol is a polar molecule with a hydrogen attached to an oxygen (contains an alcohol functional group); therefore, ethanol is able to hydrogen bond. Thus, a corresponding sensing material that would show affinity to ethanol should also be polar and ideally be able to hydrogen bond. Polymers that fall into this category are, for example, polymers containing alcohols, amines, and carboxylic acids.

Choosing a polar polymer for ethanol does not considerably narrow down the choice of polymers, since many polymers are polar and also have the ability to hydrogen bond. Since ethanol is a small molecule, polymers with shorter side chains, which have the ability to pack tighter (smaller interstitial spaces between the polymer chains), may be a superior choice since the closely packed polymer chains act as a filter, keeping larger interferent molecules out of the polymer matrix. Bulky side chains may also be used, which keep larger interferents away due to steric interactions.
Sensing materials may also be modified by the addition of dopants, a small amount of a desired material used to improve a material’s properties. Dopants in sensing materials are typically either metals or metal oxides; however, other compounds such as acids may also be used. A dopant may be added to improve the sensitivity and/or selectivity of a sensing material. In this case, a metal or metal oxide should be chosen that is able to coordinate (via metal coordination) with the target analyte (ethanol).

The other key consideration is the type of sensor. For example, a microcantilever responds to added weight; a capacitive sensor responds to an effective change in dielectric constant and/or to swelling of the polymer; and a resistive type sensor responds to a change in resistance. For a mass-based sensor, like the microcantilever, sensing site density is most important. A conductive sensing material may hinder a capacitive type sensor, whereas a conductive sensing material is required for a resistive type sensor.

Sensing materials for ethanol are selected based on how ethanol is likely to interact with a sensing material, from a mechanistic standpoint. This still results in a long list of potential sensing materials including polymers containing alcohols, amines, and carboxylic acids. To narrow down this list, the operation requirements for the final product are taken into consideration. An in-vehicle sensor must operate over a wide range of temperature between -40°C and 60°C and therefore, the glass transition temperature of the polymeric sensing material must be above 60°C. A very sensitive sensing material is needed, thus more ordered (or crystalline) polymers are better since they tend to have higher sensitivity (Fink, 2012). High selectivity is also needed. However, it is difficult to find a highly selective sensing material that solely targets one analyte. This can be resolved using a sensing array with multiple sensing materials instead of a single sensor.

Once one or a few sensing materials are chosen for a sensor, they must be evaluated experimentally to determine if they are in fact suitable for the target analyte. Polyaniline (PANI) was chosen as a sensing material for ethanol. Derivatives of PANI, such as poly (o-anisidine) (PoANI), which is PANI modified with an alkoxy side chain, were also chosen. The alkoxy functional group on PoANI may add additional sensing sites for ethanol, but may reduce the packing ability of the polymer.

Metal oxide dopants were also chosen, including zinc oxide (ZnO). ZnO is used to oxidize ethanol for catalysis and thus, ethanol is able to coordinate with ZnO. Therefore, dopants such as ZnO should attract ethanol and thus, improve the sensitivity of the polymer. To determine the optimal amount of dopant to use, different amounts of dopants must be tested experimentally.

From a mechanistic standpoint, PoANI was chosen because it had two functional groups (amine and alkoxy groups) that were likely to attract the alcohol group in ethanol. PoANI is both polar and able to hydrogen bond. It is also crystalline in nature and tends to pack in an orderly
and compact fashion, with the alkoxy side chain providing steric hindrance and thus, larger interstitial spaces that improve the mobility of ethanol through the sensing material. ZnO is able to coordinate well with both PoANI and with ethanol, thereby improving the sensitivity of PoANI to ethanol. ZnO also has a larger affinity to ethanol than the other interferents, which improves PoANI doped with ZnO’s selectivity towards ethanol.

The higher the amount of ethanol that sorbs onto a sensing material, the more sensitive the material is to ethanol. Results on sensitivity and selectivity will be shown at the time of the conference.

References


