How does the alcohol sensor work?

Dart chemical sensors operate by means of the fuel cell principle. A fuel cell is a chemical battery to which the fuel and oxidant are continuously supplied, so in principle it is everlasting. We should explain first what a “battery” is (strictly speaking, an electrochemical cell). Many chemical reactions consist of a transfer of electrons from one reactant to another. A simple example is the reaction of zinc with manganese dioxide. If heated together, the following reaction can take place:

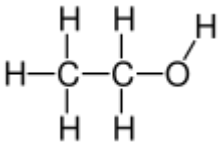
$$Zn + MnO_2 = ZnO + MnO$$

In non-chemical terms, zinc atoms, the ”fuel”, strip each manganese atom (the oxidant) of an oxygen atom. Underlying this change, is an oxidation (loss of two electrons) from each zinc atom, and a reduction (gain of two electrons) by the manganese atom. If instead of mixing the two ingredients together, we keep them separate and force the electrons to make their way along a wire to reach their destination, we have the basis of the familiar AA, AAA, PP3 batteries. To complete the electrical circuit, the zinc and manganese dioxide “electrodes” also need a connecting liquid pathway, the “electrolyte”, in the above example commonly an alkali (so the battery is known as alkaline manganese).

So much for the familiar battery. What is going on in the sensor? Well the fuel in this case is ethanol, commonly referred to just as *alcohol*, but it is just one of many. And like zinc in the above example, ethanol provides the electrons. How?

First we need to explain that the reaction requires a catalyst, strictly speaking, an electrocatalyst. The one that works best is platinum. This is coated on a porous piece of plastic which contains an electrically conductive liquid, the electrolyte, which is a strong acid. The platinum coating forms the working electrode.

The formula for ethanol is C_2H_5OH. It looks like this.



There are numerous accounts on the internet of the mechanism of ethanol oxidation on the sensor but they are all wrong, because they do not understand the difference between a chemical and an electrochemical reaction. The explanation I give here is the one which I consider best fits the evidence.

We know that each ethanol molecule provides one electron in the immediate reaction. The most reactive bond found in the molecule is the O-H so this must be the one that most likely ruptures into a hydrogen atom, and the remaining C_2H_5O fragment, which attach themselves to the surface of the platinum. The hydrogen atom then releases its electron into the conductive platinum surface. This all happens very quickly. This leaves behind a positive hydrogen ion, a proton, which attaches to a water molecule in the electrolyte to form a hydroxonium (or hydronium) ion H_3O^+. As to the remaining C_2H_5O fragment, we can only guess at its fate. Presumably it is oxidised, probably slowly, probably mainly or entirely to carbon dioxide and water. Possibly in doing so it releases further electron(s), but too slowly to figure in the main reaction which constitutes the sensor response.

So now we have formed a free electron and an acidic H_3O^+ ion and we need to deal with these. To do so, we need another electrode, also platinum, coated on the reverse side of our plastic sheet. This forms the second, counter, electrode which requires a supply of oxygen, the “oxidant”, which it draws from the air. It serves two functions. It receives the electrons by wire from the working electrode, and reacts them with water and oxygen to form hydroxyl ions, OH^-. Finally the hydroxonium and hydroxyl ions react together in the electrolyte to form water.

So how does this electrochemical reaction lead to an alcohol measurement? Well, in the breathalysers we simply count the electrons released by the ethanol molecules in a fixed volume of air. In the transdermal sensor, a continuous measurement, we count the rate at which electrons are arriving. These operations gives us the measure of their numbers which we compare with the calibration, that is to say, a result from a sample with known alcohol concentration, to obtain the desired value. And that’s it.

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