The carbon monoxide sensing challenge

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Leading developers of PEM fuel cell-based CHP systems are close to large-scale field trials of their products. They face a major barrier, however, in the lack of a carbon monoxide sensor suitable for monitoring CO levels in the reformate. Collaboration between developers may be the way to solve this problem in a cost-effective manner.

The need for a CO sensor

Of the various fuel cell technologies currently in development, the low temperature technologies are closest to market for many applications. Of the low temperature technologies, hydrogen fuelled PEM fuel cells currently achieve the highest electrical efficiency levels. As a result they are likely to be the prime stack technology used in applications like combined heat and power (CHP) and automotive, where high electrical efficiency is of prime importance. If hydrocarbons are used as the primary fuel, a reforming process is needed to convert hydrocarbons into the hydrogen rich gas required by the fuel cell stack. This reforming process inevitably generates carbon monoxide. Additional process steps, such as water gas shift reactors, preferential oxidation reactors and methanation are used to reduce CO levels as far as possible.

While the holy grail of fuel cell research is the development of a CO tolerant stack technology, current and forthcoming PEM fuel cells are still highly sensitive to CO poisoning. This leads to a performance drop and ultimately limits fuel cell lifetime.

Knowing the CO concentration in the gas supplied to the fuel cell is important for a number of reasons:

- to prevent permanent damage to the fuel cell stack;
- to minimise loss of electrical efficiency due to excess air supply to the preferential oxidation reactor;
- to monitor performance of the fuel preparation process; and
- to control reforming process start-up.

Cambridge Consultants has surveyed the market to identify the CO sensing requirements and the suitability of existing technologies, in order to explore possible ways of addressing this clear technical need.

There are many CO sensing systems available, for applications ranging from workspace safety to exhaust gas analysis. The problem is that there none are currently able to measure CO concentrations in a hydrogen rich gas to sufficient accuracy at a cost level suitable for application in a domestic fuel cell CHP system.

Existing commercial technology

The sensing technologies currently used for CO measurement are:

Technique	**Typical application area**
Infra-red absorption	Gas analysis for combustion processes and chemical plants, environmental analysis
Electrochemical cells	Workspace monitoring, industrial sensors
Semiconductor sensors	Residential CO detectors
Reagent gel sensors	Workspace CO exposure monitors
Flame ionisation (in combination	Gas analysis for process plants

with methanising catalyst)	

Infrared (IR) absorption techniques rely on measuring the absorption of infrared light in frequency bands characteristic of CO. The carbon monoxide bands are distinct from those of most other common gases and therefore this technique can provide good specificity, except in the presence of water vapour, which is a strong interferrent. Sample drying is therefore often required since relative humidity levels of the reformate are close to 100% in many applications. Costs for infrared sensing systems are often well above €1000, largely due to the high cost of IR sources and detectors.

Electrochemical cells for CO sensing are mass-produced, widely used in health and safety applications like monitoring of CO concentration in workspace environments, and in fire alarms. The cost for these sensors would be reasonable for a fuel cell system application. The main drawback, however, is that since the electrochemical process occurring in these cells is the oxidisation of CO, there is an inherent cross sensitivity to other reducing gases such as hydrogen. Even products which claim low cross sensitivity to other gases will provide insufficiently accurate CO readings when measuring CO in a gas mixture which contains 3 to 4 orders of magnitude more hydrogen than CO, as is the case in most fuel cell applications.

Solid oxide semiconductor surfaces are also widely available and low cost. These sensors also oxidise carbon monoxide, with the change in adsorbed oxygen concentration on the semiconductor surface leading to a change in resistance. Consequently they also suffer from the hydrogen cross-sensitivity problem, making them similarly unsuitable for the fuel cell application.

Reagent gel sensors are used in detector badges for personnel in toxic environments, as well as in residential sensors. They contain a sol-gel entrapped colour reagent for the relevant gas, deposited as thin layers onto a piezoelectric polymer film. The measurement involves illuminating the reagent spot with light of a suitable wavelength, which generates heat proportional to the colour change that has been created chemically within the reagent layer. This heat expands the piezoelectric film, producing an electric charge that can be measured. The main disadvantage of this approach is the slow recovery time, which does not allow dynamic monitoring.

Flame ionisation detectors (FID) are commonly used for the measurement of hydrocarbon concentrations. When a sample gas is added to a hydrogen flame, the electrical resistance between two electrodes in the flame is linked to the hydrocarbon concentration in the sample gas. If the CO contained in the sample is converted into methane using a methanation catalyst, CO concentrations can be measured with high accuracy. In the stationary fuel cell application there are already hydrocarbons present in the reformate, due to methanation of CO in the fuel preparation process. Therefore two FID measurements would be required to distinguish between hydrocarbons already present in the reformate and hydrocarbons resulting from the methanation of the CO content in the sample. Furthermore the precise hydrogen mass flow feeding the flame has to be known. This would require either extracting purified hydrogen from the reformate and metering it accurately into the FID, or a separate bottled supply of clean hydrogen. This together with a cost of current laboratory systems above the €10000 mark make FID based CO detection unattractive for use in fuel preparation for fuel cells.

Upcoming technologies

There are numerous research programmes investigating alternative techniques for carbon ~~dioxide~~ monxide monitoring.

Some of these are focussed on extending the operating range of the sensors to higher temperature and relative humidity. Technologies under investigation include: acoustic wave-based microsensors, catalytic gate field effect transducer (FET) sensors, and thin film transitional metal oxide solid-state sensors.

Other approaches are aimed at reducing the hydrogen cross sensitivity. One promising approach is to use a mini-PEMFC, with a fixed load, as the sensor. The reduction in output current is correlated to the cumulative CO concentration passing through the cell, and is not affected by hydrogen (provided sufficient H_2 and O_2 are present for full power operation). Unlike a normal fuel cell, these mini-cells are being designed to have enhanced sensitivity to CO poisoning, but also to be capable of being fully purged of accumulated CO on a periodic basis. Current development work shows good promise although both response time and sensor size need to be further reduced.

Other areas of investigation for CO-specific sensors include tuning of electrochemical cells by modifying the applied bias potential, and the measurement of resistance change of copper chloride films on exposure to carbon monoxide. The latter is an example of how CO can be selectively removed from the gas stream by an interaction that also causes a measurable physical effect. Cambridge Consultants has also recently been exploring other ideas for creating easily measurable physical effects from a selective CO adsorption.

A call to action

Despite the research, there is still no low cost, off-the-shelf carbon monoxide sensor suitable for PEMFC systems available. It appears that sensor manufacturers currently find this niche market unattractive, both due to the relatively small volumes and to the risk that the development of CO-tolerant stacks will eventually obviate the need for such a sensor. In the meantime though, fuel cell manufacturers and systems integrators are left with an urgent need for a CO sensor, at the very least for upcoming field trials, if not ultimately for their serial products.

In the short term, it may be that a compromise is necessary. While there seems little prospect of any near-term sensing solution meeting the cost targets for serial production, there may be system solutions that can provide a practical measurement at a cost of a few hundred Euros - still painful, but perhaps not completely out of reach for field trial units. Such systems solutions would combine an off-the-shelf sensor with some pre-conditioning of the reformate and potentially additional measurements and signal processing.

In the longer term, if the industry wants to ensure that a low-cost sensor becomes available, it may need to push the development itself. A bespoke sensor development program might be beyond the means of most individual CHP fuel cell system developers and, despite its importance, the ability to measure CO concentrations is not seen by any of the integrators we spoke to as key to product differentiation. But under these circumstances, there is a strong case for a collaborative development effort, supported by a number of fuel cell developers and integrators. This approach would reduce the risks and costs to any individual company, while removing a major obstacle on the way to market introduction.

It might seem odd for companies in direct competition with each other to collaborate on a potentially critical technical breakthrough. But when a totally new market is being created, especially one that needs to reach critical mass to be viable (as is the case to a large extent with combined heating and power), collaboration makes a lot of sense. Carbon monoxide sensing in fuel cell systems is not an impossible problem to solve. A united push from the CHP industry could create the momentum needed to move solutions from laboratory to production and bring the market one step closer to reality.

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