Fuel Cell Technology:
Analyzing Sulfur Levels to Improve Efficiency

article

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Loading Total Sulfur XVI+ Analyzer with Lead Acetate Tape

Fuel Cell Technology is a new efficient alternative to fossil fuel combustion for producing electrical power and has the additional benefit that it does not pollute the environment. The Proton Exchange Membrane Fuel Cell (PEM) has the broadest potential array of applications with fuel cell technologies; yet, it is sensitive to a wide range of impurities, especially sulfur. The lifetime of fuel cells is mostly dependent on the impurities in the feedstock, such as sulfur. Recent developments have demonstrated that it is possible to make the feedstock for the fuel cell practically sulfur-free by using a desulfurization unit. A total sulfur analyzer records the sulfur concentrations in the outlet stream of the desulfurization unit over time - producing "breakthrough curves". As a result of these measurements the quality (residual sulfur) and the capacity (life cycle time) of the desulfurization unit are evaluated. Breakthrough curve measurements require not only high sensitivity but also excellent stability. There are some important considerations for the laboratory and chemist to control the reproducibility and the detection limits of the analysis. Only in-depth analyses can provide information about the factors which significantly affect the measurements.

Fuel Cell Technology

The demands for energy are growing daily while conversely the production of petroleum and natural gas is declining rapidly due to falling reserves of crude oil. If it is possible to use the energy more efficiently, petroleum and natural gas reserves can be relied on for a much longer period. This would also result in less pollution to the environment.

A fuel cell is an electrochemical energy conversion device that converts the chemicals hydrogen and oxygen into water, and as a result produces electricity. The technology is known for its high efficiency. The Proton Exchange Membrane (PEM) fuel cell has the widest range of applications and thus is subject to extensive research. However, hydrogen is difficult to store and distribute due to problems of diffusion and explosion risks. Consequently it is necessary to use a specialized high pressure storage tank. This problem is addressed by utilizing a reformer. A reformer turns hydrocarbon or alcohol fuels into hydrogen, which is then fed into the fuel cell. The reformer extracts hydrogen from hydrogen-rich fuels like methanol, natural gas, petroleum, gasoline and even biogas or biodiesel and then directly feeds the hydrogen gas to the fuel cell.

The heart of the PEM fuel cell is the platinum ruthenium anode-catalyst (figure 1) however this is very sensitive to impurities like sulfur and can easily be damaged. If hydrogen is to be produced from hydrogen-rich fuels using a reformer, the sulfur in the hydrocarbon fuels must be removed from the feedstock to extend the lifetime of the fuel cell. During this stage of the process, a total sulfur analyzer may be used to analyze the sulfur content of the hydrogen that is produced. The Center for Fuel Cell Technology Ltd. (ZBT GmbH) has great expertise on preliminary and subsequent process steps for hydrogen production and gas purification. ZBT investigates different materials for the development of a highly efficient modular desulfurization unit.

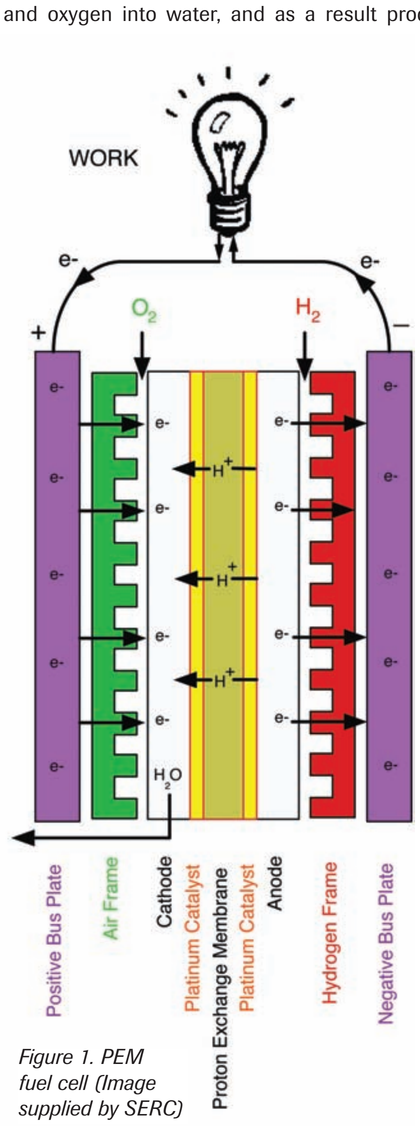
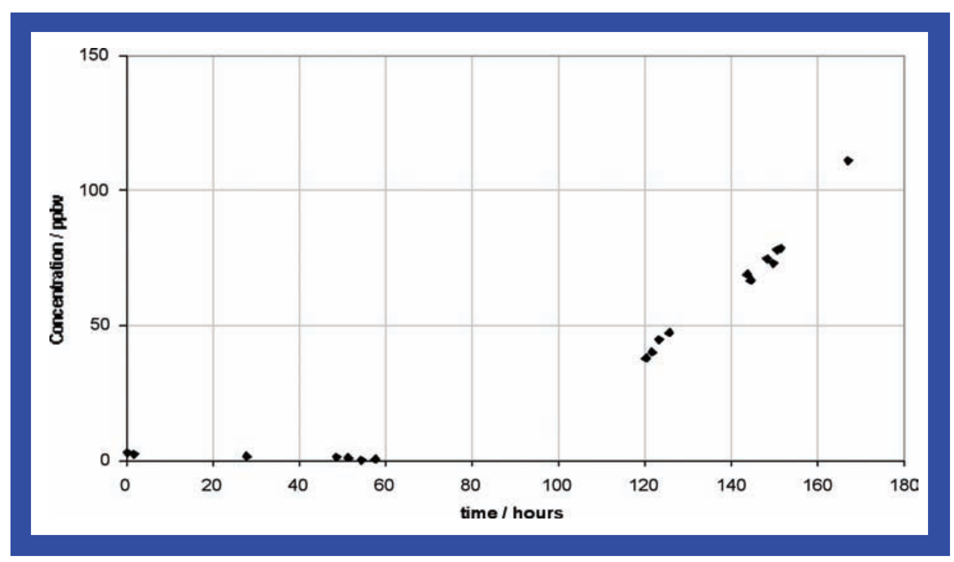


Figure 1. PEM fuel cell (Image supplied by SERC)

Desulfurization

The quality of a desulfurization unit is based on two characteristics:

1 Residual sulfur concentration -
How much sulfur is contained in the outlet stream of the desulfurization unit.



Graph 1. Breakthrough curve of a desulfurization unit

2. Capacity - How much sulfur the unit can handle until it reaches a predefined sulfur concentration.
A breakthrough curve shows the sulfur concentration in the outlet stream of the desulfurization unit over time. Also the shape of the breakthrough curve is of special interest in order to estimate the tolerance or robustness of the desulfurization unit.

These characteristics are measured in "breakthrough studies". For example, a unit should desulfurize a gas stream containing 500 ppbv H_2S. A total sulfur analyzer monitors the sulfur concentration in the outlet stream. Graph 1 represents a typical breakthrough curve.
The chart shows extremely low sulfur concentrations during the first 60 hours. After this the concentration increases asymptotically until it reaches the input concentration. Graph 1 shows the measurements during 170 hours where the experiment ends. At this point the sulfur concentration reaches a typical threshold level of 100 ppbv, .

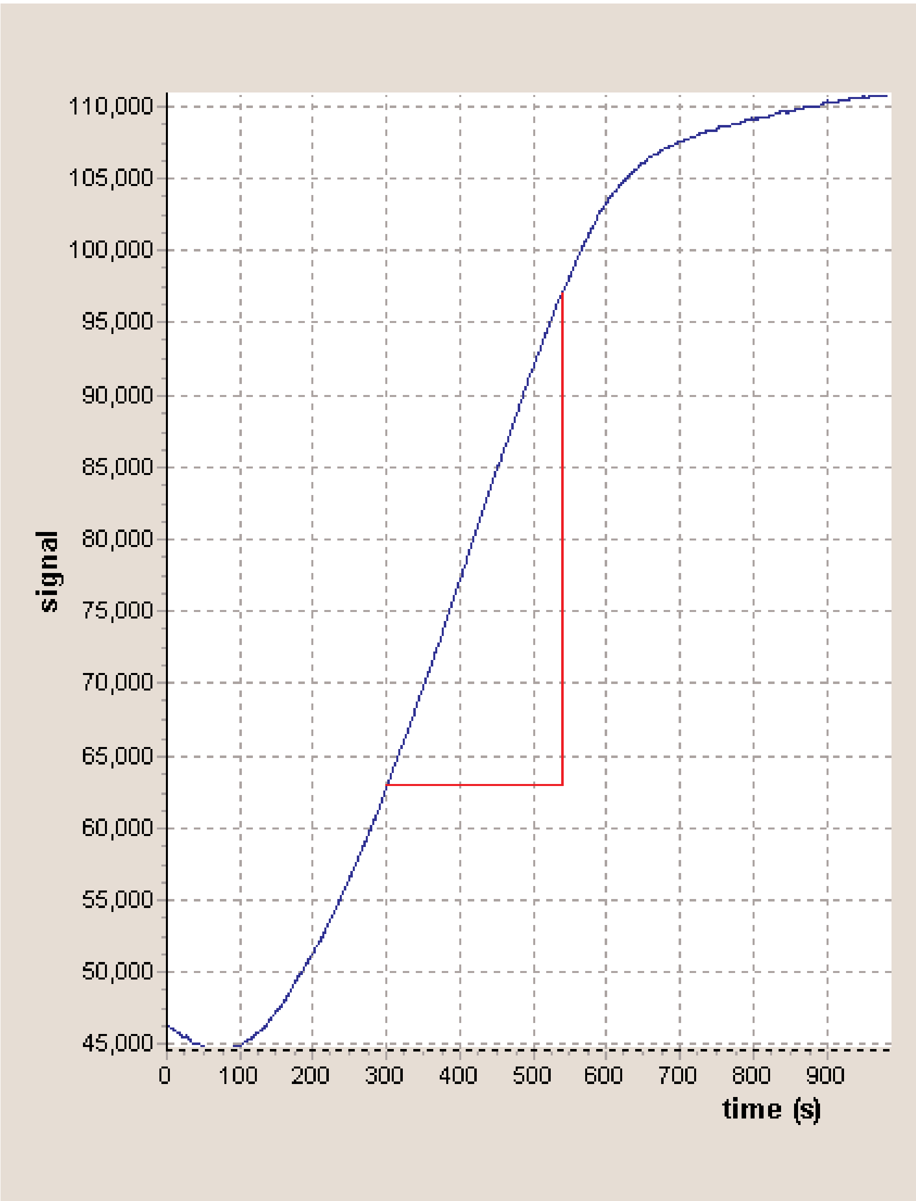
To do a breakthrough curve measurement within a reasonable time, the experimental conditions are different from the normal working conditions. In this case the space velocity (gas flow rate divided by volume of catalyst) is 5 times higher and the inlet concentration is 2 times higher than under realistic conditions. With the results it is possible to predict the lifetime of the desulfurization unit for many applications with less demanding conditions. Since the breakthrough curve depends on the equilibrium, kinetics and absorption capacity, the predictions are done by computer simulations.

Sulfur analysis

Since the typical sulfur levels in the outlet stream of the desulfurization unit are very low the total sulfur analyzer must have high sensitivity in order to determine the concentrations accurately. (sub-ppb levels). ZBT GmbH uses the Total Sulfur XVI+ Analyzer, (Thermo Electron Corporation). This analyzer uses the lead acetate tape detection principle:

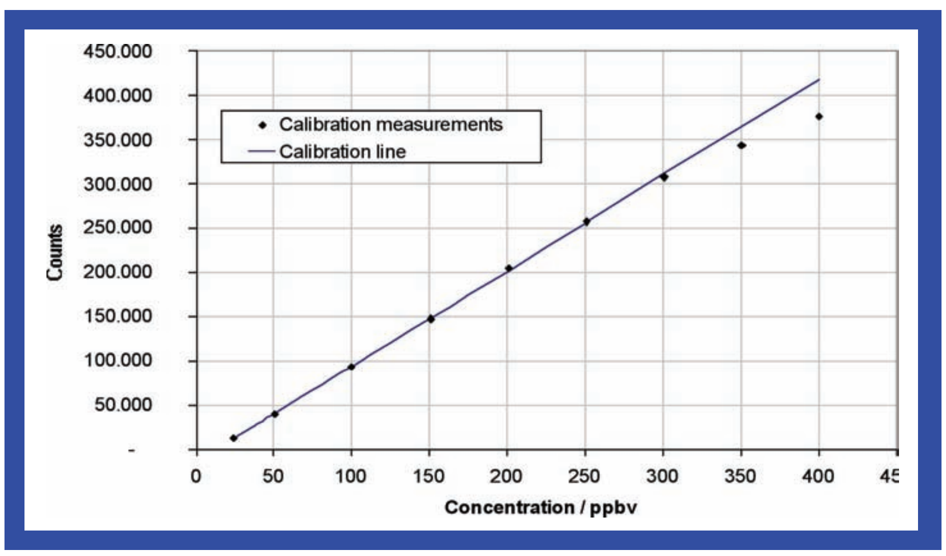
$$H_2S + Pb(CH_3COO)_2 \xrightarrow{H_2O} PbS + 2\,CH_3COOH$$

Lead acetate, $Pb(CH_3COO)_2$, is a white salt. Light illuminating the tape reflects on the white surface and a photodiode detects the reflected light. The H_2S reacts with the lead acetate to produce lead sulfide (PbS) which forms a dark brownish stain on the white tape. Less light reflects when the color of the tape changes from white to brown due to H_2S. The decreasing amount of reflected light is proportional to the amount of sulfur in the sample. The computer program records the signal and produces an absorbance curve (graph 2). The measurement can be the rate of color change or the total change of color, according to the ASTM D4045, D4084, D4323, D4468, D6212 and D6313 standard methods.



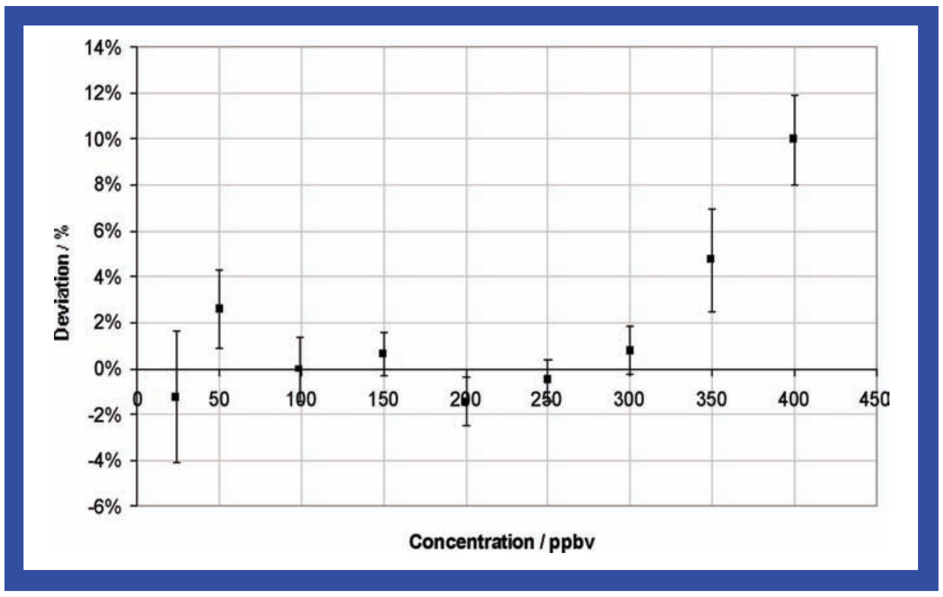
Graph 2. Typical detector response

To measure the sulfur content in the outlet stream of the desulfurization unit the total sulfur analyzer needs to be calibrated. Diluting a certified 10 ppmv H_2S gas with pure hydrogen gives a set of calibration standards. Graph 3 shows the correlation between the detector signal and the concentration of H_2S. Each point represents the mean value of three measurements.



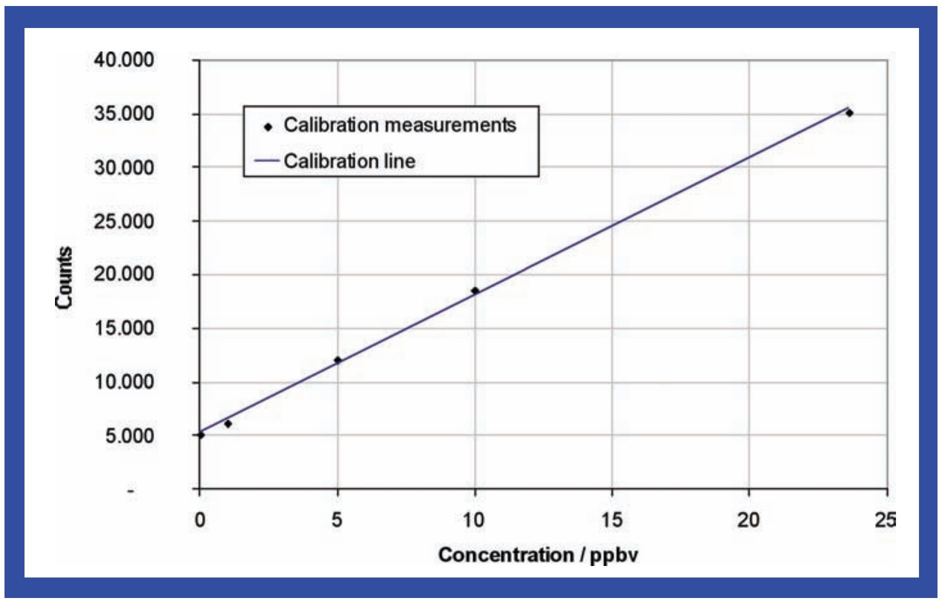
Graph 3. Calibration curve of H_2S in hydrogen

The calibration fits to a linear correlation up to 300 ppbv under optimized measurement conditions for the XVI+. This calibration curve is valid for measurements in the range of 25 to 300 ppbv. Error analysis is plotted in graph 4. The uncertainty is within ±3% in the range up to 300 ppbv.



Graph 4. Relative deviation plot of calibration measurements

This high level of reproducibility extends the possibility for extreme low level sulfur analysis. As a consequence ZBT has examined the response of the Total Sulfur XV1+ Analyzer to H_2S concentration from 1 to 23 ppbv. Graph 5 plots the calibration line for this concentration range.



Graph 5. Calibration curve for sulfur concentrations at sub-ppb level

To achieve such low sulfur level measurements it is very important to have full control over the analysis. During the preparation of the calibration gases the chemist should take extra care to work cleanly and precisely. Also extreme care is necessary in relation to the temperature and pressure of the samples. Since the samples are gases, fluctuations on pressure and temperature increase the standard deviations of the measurements, giving more uncertainty about the results and degrading the detection limit. Studies at ZBT GmbH even show significant effects on the data caused by flow fluctuations in the laboratory ventilation system in which the exhaust of the analyzer is fed.

Conclusions

A wide application of fuel cells mainly depends on the ability of decentralized generation of hydrogen by a reformer. The hydrogen generated must be free from impurities like sulfur to extend the lifetime of the fuel cell. Desulfurization units can reduce the sulfur concentration in the hydrogen stream to almost zero. With breakthrough curve studies and computer simulations the lifetime of a desulfurization unit can be predicted. Since the sulfur concentration in the outlet stream of the desulfurization unit is down to sub-ppb level, the breakthrough curve measurements rely on a very sensitive and accurate total sulfur analyzer. The Total Sulfur XVI+ Analyzer (Thermo Electron Corporation) consists of a sophisticated detector which can measure sulfur concentration as low as 1 ppbv and is applicable for advanced laboratories for fuel cell technologies.

About Thermo Electron Corporation's Total Sulfur XVI+ analyzer

The XVI+ analyzer has been developed to provide the petrochemical, automotive and food and beverage industries with a complete solution for fast and accurate low detection analysis.

In addition to offering a completely versatile solution – the XVI+ can analyze liquid and gas/LPG samples from very low levels (ppb) to high concentration (ppm) – the lead acetate detection methodology contained within the instrument has several immediate notable advantages:

- It is the only known method capable of determining H_2S without any interference making the XVI+ Analyzer H_2S specific
- It allows the XVI+ Analyzer to measure total color and color change rates

Thermo's XVI+ Total Sulfur Analyzer has been engineered to optimize the analysis of sulfur, especially in extremely low concentrations. The novel lead acetate detector ensures unparalleled levels of accuracy. TheEuS Analytical Software streamlines all aspects of the analysis enabling scientists to achieve routine total sulfur analysis in an efficient, fast and reliable way. Clear icons enable the user to operate the instrument at a glance. The software has been configured to allow the operator to multi-task without affecting the analyses in progress. Thus, sample queues can easily be modified or data and calibration lines independently evaluated. Results are typically presented in customized print reports or exported in a variety of data formats.