

The Electrochemistry of Gases: New Sensing Opportunities

by Emory S. De Castro

Electrochemistry on gases originated in 1839 with Grove's "gaseous voltaic battery"¹. Over 90 years later, Bacon built a demonstration fuel cell consisting of porous nickel electrodes². He is credited with creating a stable three phase reaction zone of electrode, gas, and electrolyte. Today's fuel cell electrodes are far more sophisticated^{3,4}, and lend themselves to other important electrochemical processes. For example, the electrolytic production of pure hydrogen and oxygen is possible through an SPE® (solid polymer electrolyte) stack where DuPont's Nafion® cation exchange membrane is the electrolyte⁵. Other processes include gas purification⁵, inorganic salt splitting (caustic from soda ash)⁶, or even synthetic applications (electrocatalytic oxidation of ethylene and methane)⁷. This review will show how the three-phase region of fuel cells can be exploited to create electrochemical gas sensors.

Gas Diffusion Electrodes

Contemporary gas diffusion electrodes (GDEs) make use of high-surface area supports for metal catalysts, as well as solid inert materials with high gas permeability. Figure 1 shows a sketch of a GDE consisting of carbon black and PTFE pushed against a porous current collector. The gas can either pass through tortuous pores in the assembly or within the Teflon® support. The hydrophobic PTFE inhibits aqueous solutions from completely penetrating the structure but the carbon black support is still capable of being wetted by electrolyte. Although direct electrochemistry on a gaseous species is still limited by the gas-liquid solubility, the solution layer can be thought of as a thin meniscus and thus capable of supporting very high gas flux rates.

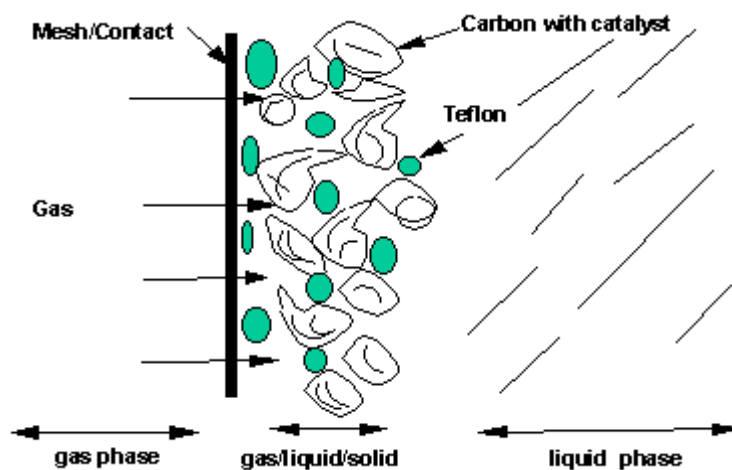


Figure 1: Schematic Representation of a Gas Diffusion Electrode

For the fuel cell program, one additional advancement involved the elimination of the liquid electrolyte. In 1957 Grubb realized that the liquid electrolyte in a GDE could be replaced by a solid, ionically conductive polymer⁹. Thus, whole electrode-electrolyte assemblies consisting of porous electrodes and ion-exchange polymers were manufactured. These assemblies are variously called "MEAs" for membrane electrode assembly, "SPEs" for solid-polymer electrolyte, or "PEMs" for proton exchange membrane. These three acronyms refer to use of an ionically conducting membrane as an integral element in a device. We will use "GDE" to mean assemblies similar to Figure 1 and "MEA" to mean electrode assemblies directly deposited on an ionically conductive membrane.

Why Employ GDEs or MEAs as Sensors?

For current-generating measurements, electrode surface area can be one advantage. As seen in Figure 1, the surface area that is inherent in most GDEs and MEAs can lead to an apparent current amplification ranging up to around 100 times that obtained on an equivalent simple geometric area. Both voltage- and current-measuring sensors gain from incorporating a ready gas-liquid-solid interface into the electrode element itself. The disadvantage of being limited by gas solubility in the electrolyte is offset by the very thin diffusion layer formed with the wetted electrode surface. This thin layer can support high flux rates. Conductivity-based sensors can also benefit from having a thin "solid electrolyte" as part of the sensing element.

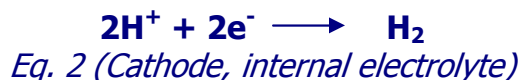
Breathalyzers to Check Gasoline

An early use of an acid electrolyte and a platinum - Teflon GDE was for detection of ethanol in breath¹⁰. An interesting use adapting the ethanol detector is for adulteration of gasoline by kerosene¹¹. Various oxygenates (e.g. methanol, ethanol, isopropyl alcohol, and butyl alcohol) are added to gasoline in order to alleviate problems associated with the knocking of lead-free gas. The resulting headspace analysis provides a "fingerprint" of each gas brand. One common adulterant is kerosene. Instead of a complex GC procedure, these scientists measure the resulting alcohol in the headspace and compare the total alcohol level to that obtained with unadulterated samples. They report sample throughput of 5 determinations per hour with a precision of 0.21% relative standard deviation and an accuracy of +/-0.2%.

Industrial Hydrogen Sulfide

The American Conference of Governmental Industrial Hygienists have set a time weighted average (TWA) exposure of H₂S at 10ppm and a short-term exposure limit (STEL) of 15ppm. Other European agencies have set TWA and STEL limits at

30 and 70ppb respectively. These limits can be achieved via an MEA outfitted with a porous silver anode supported on a cation exchange membrane (Nafion 417)¹². Here, one holds the sensing electrode at a potential where silver would not ordinarily be oxidized unless hydrogen sulfide is present. On the other side of the MEA a solution of 10mM HClO₄ / 1M NaClO₄ contains a Hg/HgSO₄ sat. Na₂SO₄ reference electrode and a platinum counter electrode. Protons liberated from the silver-sulfide reaction migrate through the cation exchange membrane and eventually are reduced to form hydrogen. The overall reaction is summarized in Equation 1 and 2.



By using acidic media, unwanted trapping and saturation of electrolyte with sulfide ions are eliminated. The use of the MEA reduces the response time of the sensor since the reaction occurs at the membrane-electrode interface, not in solution. A pH no less than 2 is used in order to minimize the oxygen reduction reaction that would cause background currents. Furthermore, since the affinity of sulfide for silver is far greater than that of any of the halides, silver halide complexes would not be detected with this sensor. A detection limit (three times background current) of 45ppb (v/v) H₂S is reported when operating in constant potential amperometric mode. By holding the potential for a period, and then scanning in a negative direction, the device is able to pre-concentrate the analyte and reduce back the silver sulfide. This cathodic stripping operation enables a detection limit of 0.07ppb (v/v). Since there is no membrane covering or solution-limited diffusion, the response time is quite fast: 0.5s for a 95% full current (amperometric mode). Coupled with a reported 2 month stability under constant operation, this device appears appropriate for real-time industrial monitoring.

In the Operating Room

Most anesthetics are administered as gaseous mixes, and thus dosage levels need to be monitored continuously. For example, a gas diffusion electrode was adapted as a thin-layer coulometric cell for the analysis of nitrous oxide in air¹³. The use of a fixed, small volume cell enables exhaustive electrolysis of the trapped gases. If one has previously characterized the system, coulometric analysis (integration of the current to accumulate total charge) can be employed as an *absolute* technique. That is, no reference analytes are used to calculate concentration. Charge is directly related to moles of analyte electrolyzed. A gas sample is

introduced into a thin layer cell, a constant potential is applied via three electrode control, and the resulting charge is monitored until a constant level is recorded. This technology can perform a multicomponent analysis of oxygen and nitrous oxide after judicious selection of the reduction potential. Typical thin-layer volumes are under 1mL and often range from 60 - 100L. The high surface area of the GDE combined with the low sample volume make for short electrolysis times.

How Safe is your Furnace and Fireplace?

The danger of carbon monoxide in the home has led to numerous electrochemical sensor de-signs. For example, the use of an MEA without any additional electrolyte was demonstrated by Yasuda et al.¹⁴. Three electrode strips comprising a platinum working, gold reference, and platinum counter are deposited on an insulating alumina substrate. A thin film of Nafion is cast over the ensemble of electrodes. By maintaining a constant potential of 0.4V vs. gold reference, they are able to oxidize carbon monoxide to carbon dioxide. Current is then proportional to CO concentration. Although this design is amenable to mass production via methods similar to circuit board technology, the sensitivity is limited by the diffusion of CO through the Nafion film, as well as instability of the gold reference electrode. Amperometric gas sensors based on GDEs, MEAs, etc. have been reviewed¹⁵.

Amperometric versus Potentiometric Sensors

We have shown several approaches for incorporating three-phase zones into sensing strategies. In general, the electrode is either part of a conducting membrane that serves as the electrolyte or a barrier to solution components, or the electrode is a composite of materials that allow gas and solution to permeate to the same site.

Practical commercial amperometric systems often fall short when power and lifetime are issues. Since amperometric systems consume current, they have an inherent limitation. The larger the electrode, the greater the signal, the more power they consume. Also, since these are electrolytic devices, the accumulation of reaction products sometimes change the chemistry at working, reference, or counter electrodes. Potentiometric sensors can often overcome these limitations, since potentiometric measurements are based on the potential difference between two electrodes at zero current. While zero current is never actually obtained, potentiometric measurements are often made at nA-fA levels.

For potentiometric measurements the extended surface area of GDEs is not exploited: these measurements are area-independent. However, the three-phase region can be used to advantage in potentiometric gas sensors. For example, the Electrosynthesis Company has developed a unique potentiometric gas sensor for carbon monoxide based on gas diffusion electrodes^{16,17}. In Figure 2, the central

section is an inert spacer filled with concentrated acid while the ends are conductive plastic. The backside section is covered to create a reference gas space. A voltage is measured between the two electrodes. Once the sensing half is exposed to carbon monoxide, a reaction with the platinum catalyst produces a voltage change compared to the reference "clean air side". This sensor produces ample signals over 10-400ppm CO, and is suitable for home consumer use or for portable field devices. Furthermore, the cost of parts is low enough to allow the whole package to be competitive with currently available technology while the minimal current drain allows operation for over one year.

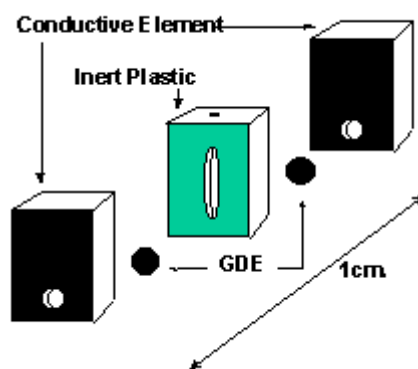


Figure 2 - Potentiometric CO Sensor

Potentiometric Sensors for Long Term Monitoring: Medical Applications

The measurement of physiologically important parameters like carbon dioxide and ammonia has been demonstrated through potentiometric PEMs as well. Meyerhoff and associates have reported the use of an ion-exchange membrane as an internal sensing element along with internal buffer solutions¹⁸. The goal of this work was to create disposable transducers with fast response times for use in flow-through analyzers.

However, for actual respiratory monitoring, one would prefer a sensor with a response time of 200ms or less. By depositing porous layers of IrO₂ and Ag on a silicon substrate containing micro-machined pores, and coating one side of the assembly with a conducting gel (Promeon from Medtronic), Tierney and Kim were able to create a potentiometric sensor for CO₂¹⁹. The conducting gel is first conditioned in KCl and NaHCO₃. Iridium oxide responds to changes in pH. The iridium oxide electrode follows changes in the gel as CO₂ displaces the carbonate equilibrium. Although the authors report a "best" response time of 900ms through the assistance of an enzyme carbonic anhydrase, this is an improvement of several orders of magnitude over conventional Severinghaus-type CO₂ sensors.

GDEs as a Construction Element

For some, the use of gas diffusion electrodes lies not in direct electrochemistry on a gas but more as a construction element allowing easy access to a plentiful reagent. There is still activity on portable glucose monitors for diabetics. The enzymatic reactions behind the determination often involve a ready supply of oxygen. By immobilizing glucose oxidase as part of a gas diffusion electrode, and using the electrode to monitor the reaction products (H_2O_2) of the enzyme reaction, Kaisheva et al. have created a system no longer limited by oxygen solubility in solution²⁰. Scientists at Nova Bio-chemical have patented a multilaminate device using similar concepts²¹. Newman et al. have applied modern screen printing techniques to develop a Nafion MEA for glucose²². They use rhodium modified carbon as the ink to create a mass-produced device that maintains sensitivity even in complex fermentation media.

Commercially Available Sensors based on GDEs

The use of GDEs, etc. is not limited to research or industrial development. Many gases are currently being determined by commercially available units employing GDEs or MEAs. Table 1 shows several examples of these. For those applications listing "battery" under method, the sensor is actually run as a current-generating fuel cell whereby the current is directly proportional to the gas concentration.

Analyte	Sensor/Method	Vendor
O_2	GDE/Battery	Teledyne, CA
O_2	GDE/Battery	Delta F, MA
CO	MEA/Amp erometric	Neotronics, GA
H_2S	MEA/Amp erometric	Neotronics, GA
SO_2	GDE/Amp erometric	Neotronics, GA
Cl_2	GDE/Amp erometric	Neotronics, GA
NO_2	GDE/Amp erometric	Neotronics, GA
$EtOH$	GDE/battery	Lion Laboratories, UK

Table 1 - Commercially Available Sensors

The Future

Mass production via circuit board technology will lead to the development of single packages capable of measuring multiple gases. Hydrogen, oxygen, carbon dioxide, and ammonia have reported to be amperometrically determined at a single sensor package²³. This four-analyte feat is accomplished by laying down a strip of platinum and palladium for electrolyzing oxygen and hydrogen by applying 0V and 0.35V respectively vs. another strip of Ag/AgCl that serves as a reference. These two strips are coated with a thin layer of a cation exchange membrane. At a different zone, an anion-exchange membrane and copper strips are used to measure carbon dioxide and ammonia at -1V and 0.1V vs. the Ag/AgCl respectively. A response time of 60 seconds is reported. Undoubtedly, as the need for small, multi-analyte environmental sensors grows, this approach will be more commonplace.

Conclusions

We have surveyed a variety of determinations that gain advantage through the use of GDEs, MEAs, or similar assemblies. Although any sensor must be qualified under the specific application's requirements of speed, selectivity, sensitivity, and cost, the ability to perform direct electrochemistry on a gas allows scientists and engineers an added degree of flexibility in designing systems. Many of the methods and techniques outlined here are amenable to mass production, miniaturization, and incorporating multiple sensing sites for providing more complete analysis in complex environments.

References

1. Grove, W.R.; *Philosophical Magazine*, **1839**, 14, 127.
2. Crowe, B. J.; *Fuel Cells*, NASA Publication SP-5115, **1973**.
3. Yamamoto, O.; *Chem. Solid State Matter.* **1995**, 5, 292.
4. Appleby, A.J.; *J. Power Sources*, **1991**, 36, 293.
5. Oberlin, R.; Fischer, M.; *Brown Boveri Review*, **1986**, 8, 445.
6. Buhler, K.; Winnick, J.; *J. of the Electrochem. Soc.*, **1985**, 132, 2971.
7. Pletcher, D.; Genders, J.D.; Weinberg, N.L.; Speigel, E.; *U.S. Patent* 5,246,551, **1994**.
8. Shimada, T.; Kawashima, A.; Habazaki, H.; Asami, K.; Hashimoto, K; *Sci.Rep.Res.Inst.*, **1993**, 38, 63.
9. Grubb, W.T.; in Proceedings of the 11th Annual Battery and Development Conference, Atlantic City, NJ, **1957**, pp. 5-8.
10. Jasinski, R.; Salomon, M; Furumoto, Horace; *Electrochem. Contrib. Environ. Prot.*, 108-20, T.R. Beck, Ed. Electrochemical Society, **1972**.

11. Bahari, M. Shahru; Criddle, W.J.; Thomas, J.D.R.; *Analyst* (London), **1992**, 117(4), 701.
12. Schiavon, G.; Zotti, G.; Toniolo, R.; Bontempelli, G.; *Anal. Chem.*, **1995**, 67, 318.
13. Cha, C.; Liu, P. Chou, Z., Wu, Z.; Lu, W.; *J. Electroanal. Chem. Interfacial Electrochem.*, **1988**, 248, 69.14.
14. Yasuda, A.; Yamaga, N.; Doi, K.; Fujioka, T.; Kusanagi, S.; *J. Electrochem. Soc.*, **1992**, 139(4), 1091.
15. Cao, Z; Buttner, W.J.; Stetter, J.R.; *Electroanalysis*, **1992**, 4(3), 256.
16. De Castro, E.S.; et al. "Carbon Monoxide Sensor Based on Gas Diffusion Electrodes", presented at The Electrochemical Society Meeting, San Francisco, Extended Abstracts **1994**, 94-1, 1600, (abstract 1063).
17. Tomantschger, K.; et al. *U.S. Patent* 5,302,274 (**1994**).
18. Meyerhoff, M.E.; Fraticelli, Y.M., Greenberg, J.A., Rosen, J.; Parks, S.J.; Opdycke, W.N.; *Clin. Chem.* **1982**, 28(9), 1973.
19. Tierney, M.J.; Kim, H-O. L.; *Anal. Chem.* **1993**, 65, 3435.
20. Kaisheva, A.; Iliev, I; Kazareva, R.; Christov, S.; *Sens. Actuators*, **1995**, B27(1-3), 425.
21. Young, C.C.; Winarta, H.; *Eur. Pat. App.* EP 327018 A2 890809.
22. Newman, J.D.; White, S.F.; Tothill, I.E.; Turner, A.P.F.; *Anal. Chem.*, **1995**, 67, 4594.
23. Mayo, N.; Harth, R.; Mor, U.; Marouani, D; Hayon, J.; Bettelheim, A.; *Anal. Chim. Acta*, **1995**, 310, 139.

Dr. Emory S. De Castro was a Senior Scientist at The Electrosynthesis Company from 1991 to 1996. His research interests include novel gas and liquid electrochemical-based sensors, electrochemistry of transition metal complexes, and of biochemical systems. Dr. De Castro has co-authored six patents, including sensors for oxygen, carbon monoxide, and toxic metals.

The possibilities for electrochemical sensors are very broad. If you would like to discuss further the development of specific sensing devices, please contact us at (716) 684-0513, ex. 111 or e-mail info@electrosynthesis.com .