Hiden Analytical Ltd.
420 Europa Boulevard
Warrington WA5 7UN
England

T +44 [0] 1925 445 225
F +44 [0] 1925 416 518
E info@hiden.co.uk
W www.HidenAnalytical.com

Gas Analysis | DEMS
Technical Information TI-20022.2

Summary of DEMS / OEMS Options

Differential Electrochemical Mass Spectrometry (DEMS) and Online Electrochemical Mass Spectrometry (OEMS) require a diverse range of inlet options to allow analysis of both dissolved and evolved gases.

Measurement of dissolved gases is typically performed using a PTFE membrane which allows dissolved gas products to pass to the MS via a differentially pumped vacuum system.

Measurement of evolved gases is by direct analysis of product gas in a headspace with or without carrier gas flow.

This document will outline the applicability of each inlet to DEMS and OEMS applications.

Hiden Analytical DEMS Cells

Type A cell

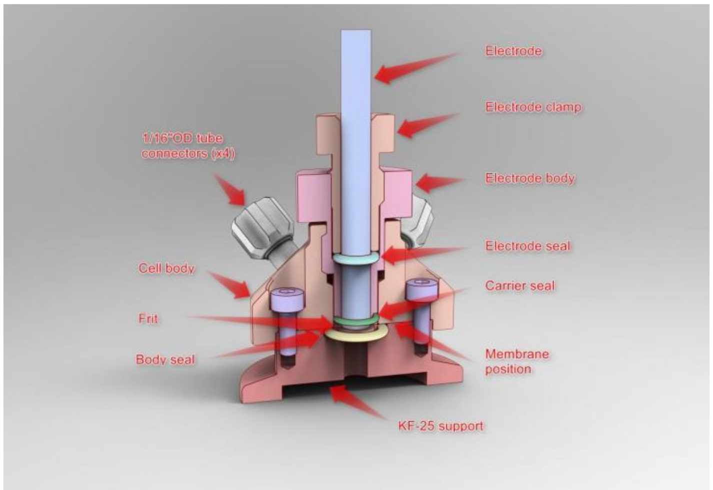

Figure 1: Type A Cell Schematic

The Type A DEMS cell is a thin layer cell, particularly appropriate for the study of desorption products under static electrolyte conditions but is applicable to many types of electrochemistry utilising an aqueous electrolyte [1].

If flow is continuous then it must be low enough that the products are not removed from the cell before crossing the thin layer of electrolyte to the MS, it is recommended to use a syringe pump delivering 1µl/s.

The cell includes a 5mm diameter vitreous carbon working electrode and 1/16" Ag/AgCl reference electrode.

Counter electrode is not supplied and can either enter the cell directly or be in contact with electrolyte outside of the cell.

Materials can be deposited onto the face of the working electrode. The electrolyte and counter and reference electrodes enter the cell through 1/16" holes.

The PEEK body and PTFE membrane allows for use of corrosive electrolytes.

Suitable for	**Not suitable for**
Dissolved gas	Evolved gas
Static conditions	High flow
Aqueous electrolytes	Volatile electrolytes
Vitreous Carbon WE	

Type B cell

Figure 2: Type B Cell

The Type B DEMS cell is a dual thin-layer cell, most suitable for monitoring continuous faradaic reactions, with controlled hydrodynamics in the determination of product formation rates and turn over frequencies [1].

Particularly suitable for CO_2 Reduction [2], the Type B cell employs dual thin layer design to compartmentalise the anode and cathode chambers using an ion conducting membrane.

The cell employs a parallel electrode configuration, high surface area electrodes and low volume catholyte layer. This gives a low cell resistance (~50 Ω), robust electrode connectivity, and minimal overpotential at the counter electrode, enabling the potentials required to produce hydrocarbons and alcohols over polycrystalline copper to be experimentally accessible.

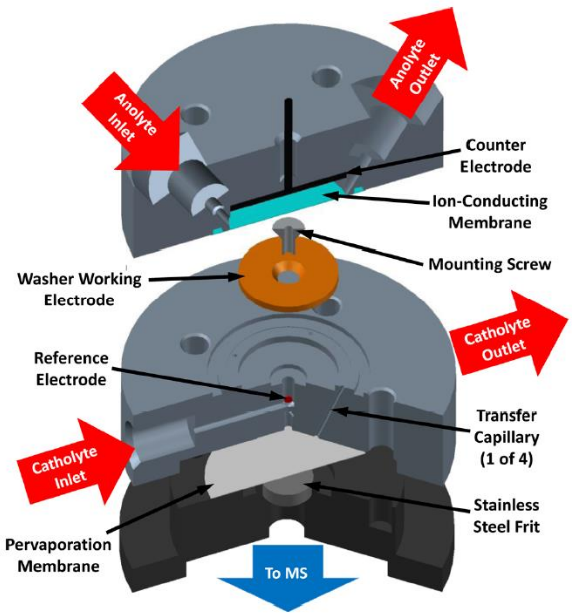

Figure 3: Type Schematic

The cell requires a low flow of electrolyte through the 2 compartments with only products formed in the cathode compartment measured by the MS. Recommended flow is 2ml/min delivered using a dual syringe pump.

Supplied with platinum counter electrode and Ag/AgCl reference electrode with options of solid Cu / Ag / Au plated or vitreous carbon working electrode.

The Type B cell is supplied with clear acrylic anode chamber to allow user assessment of bubble production but also supplied with PEEK anode chamber for corrosive electrolytes. Cathode chamber uses a PEEK body.

Suitable for	**Not suitable for**
Dissolved gas	Evolved gas
Low flow conditions	High flow
Aqueous electrolytes	Volatile electrolytes
Cu, Ag, Au, Vitreous Carbon WE	

Type B Modified Cathode Chamber

The modified cathode chamber allows for alternative working electrode materials by direct sputtering on to the membrane surface [3].

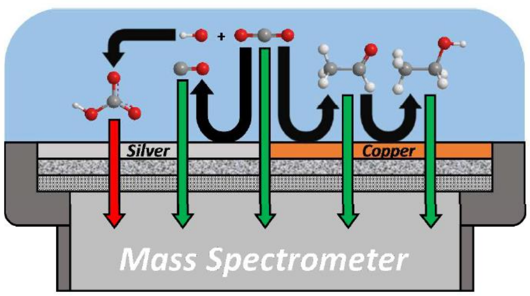

Figure 4: Direct sputtering of membrane surface

Coating the membrane surface, allows volatile species at the electrode-electrolyte interface to be sampled. Furthermore, the delay time between product generation and detection is minimized and the liquid-phase product collection efficiency is maximized.

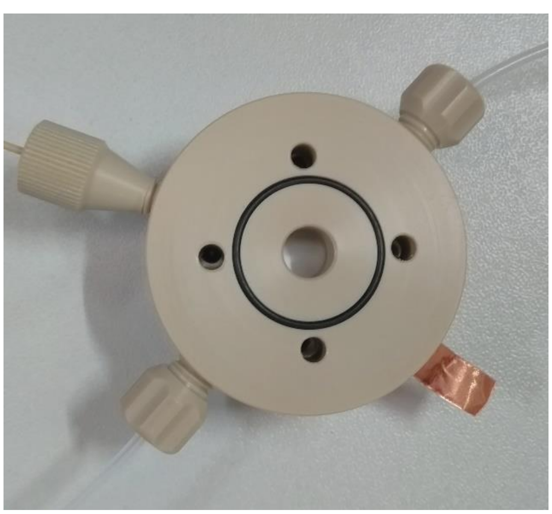

Figure 5: Modified Type B Cathode Chamber

Larger chamber volume is suitable for higher flow rates through the cell, avoiding bubble hold up.

The modified chamber utilises the same anode chamber used in the standard Type B cell.

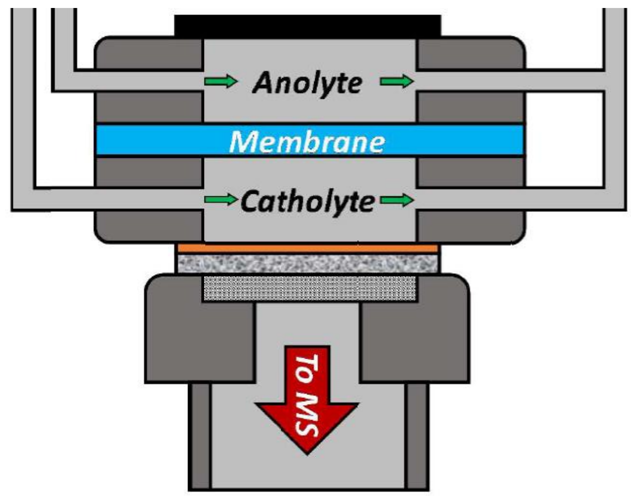

Figure 6: Schematic of Modified Type B Setup

Suitable for	Not suitable for
Dissolved gas	Evolved gas
High flow conditions	Volatile electrolytes
Aqueous electrolytes	
Sputtered WE	

DEMS Probe

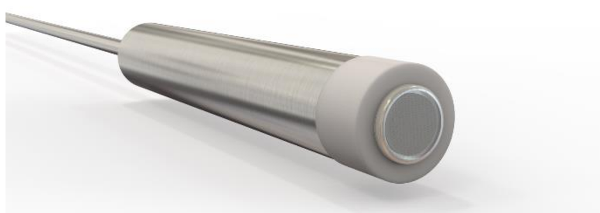

Figure 7: DEMS 6mm Sampling Probe

The DEMS probe allows dissolved gas to be measured in custom cells. The 6mm probe sits at the end of 1/16″ flexible stainless-steel tubing so can be moved between experiments easily.

It utilises the same PTFE membrane and differential pumping techniques of the DEMS cells. Changes to the instrument by-pass pumping and to the membrane interface are employed to optimise the response of the mass spectrometer to the remote probe design. A bypass pumping restrictor is employed and thicker PTFE membrane (50 microns) is used to achieve the optimum MS sampling pressure for maximum sensitivity and fast response time.

Response time is typically < 2s.

The probe should be positioned as close as possible to the WE.

The 1/16″ probe tube diameter and 6mm probe is particularly suitable for a range of Redox.me cells.

Figure 8: DEMS probe fitted inside Redox.me cell

Suitable for	**Not suitable for**
Dissolved gas	Evolved gas
Static or flowing conditions	Low electrolyte volume
Aqueous electrolytes	Volatile electrolytes
Redox.me cells	
Custom cells	

Inlets for OEMS (Online Electrochemical MS)

Ultra-Low Flow Capillary

The Ultra-low flow Capillary allows measurement of evolved gas with minimal dilution of the product gas by carrier gas flow. At 200µl/min, flow is similar to that recommended [4] for use with the ECC-DEMS cell and PAT cell from EL-Cell but is also suitable for connection to Redox.me or a custom cell.

Figure 9: Ultra Low Flow capillary connected to Redox.me cell

Corrosive resistant options make the capillary suitable for Lithium battery testing and use of volatile electrolytes.

The recommended experimental set up would allow a controlled flow of carrier gas to flow past the inlet of the cell whilst the capillary is connected at the cell outlet. This ensures carrier gas flow is set at 200µl/min.

A custom quick connect kit for the ECC-DEMS cell, allows for oxygen free cell loading and subsequent analysis, outside of an Argon box.

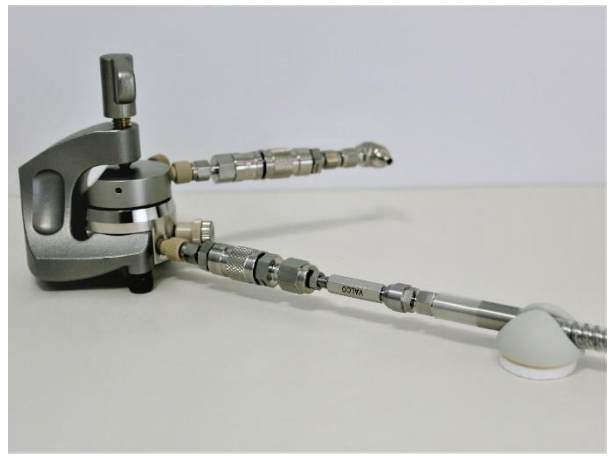

Figure 10: ULF connection to ECC-DEMS cell, with quick connects

The heated QIC inlet gives fast response and ensures condensable gases remain as vapours during sampling.

Suitable for	Not suitable for
Evolved gas	Dissolved gas
Low product gas flow	No carrier gas flow
Condensable vapours	Very low product gas flow
Fast response	Multiple streams
Various cells	
Quantitative analysis	
Volatile electrolytes	

Microflow Capillary

Figure 11: Single Microflow Capillary

For applications with only very low levels of product gas, where dilution with carrier gas may decrease concentrations below the limit of detection, the micro-flow capillary is recommended.

With flow rates of either 12 or 25µl/min, headspace gas can be sampled without significantly changing pressure in the cell.

Connection is via 1/16" fitting so is easily fitted to either custom or commercial cells.

Capillary length is either 1m (25µl/min) or 2m (12µl/min), giving response times of 8s and 16s respectively (for air). A filter helps avoid particulates blocking the capillary but because it is unheated the possibility of condensation is increased.

Option for up to 8 multiplexed capillaries to allow automated sequential sampling, from multiple sample points or cells.

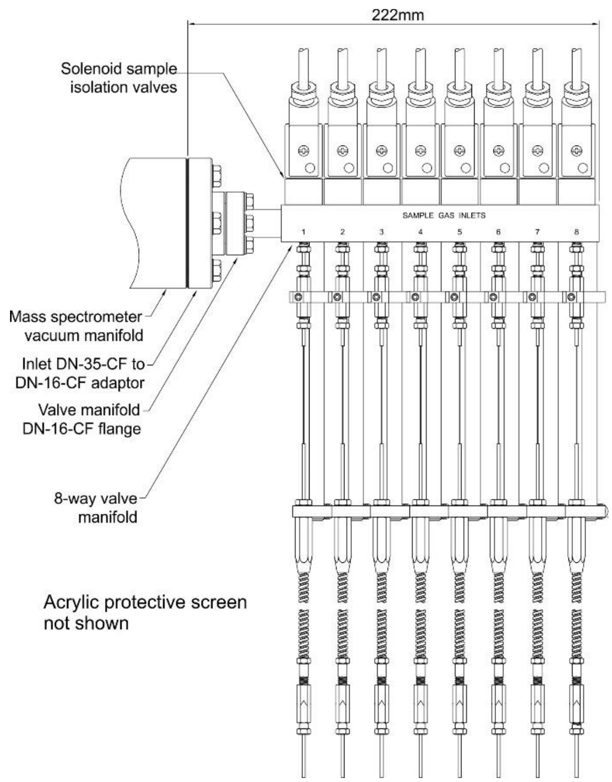

Figure 11: 8-way option for Microflow capillary

Suitable for	Not suitable for
Evolved gas	Dissolved gas
Very Low gas flow	Fast response
Multiple streams	Condensable gases
Various cells	
Quantitative analysis	
Volatile electrolytes	

Standard QIC Capillary

When cell volume or product gas levels are high then the standard QIC capillary can be used.

Flow rates from 800µl to 28ml/min are available giving fast response time (300ms) along the heated capillary. Increased capillary length (2m) gives more flexibility.

The capillary can be connected to a multistream valve so that up to 16 streams can be measured using a single capillary.

The QIC capillary flow rate can be changed easily by swapping the capillary liner and so provides a versatile solution for many applications as well as OEMS.

Suitable for	Not suitable for
Evolved gas	Dissolved gas
High gas flow	No carrier gas flow
Multiple streams	Small cell volume
Various cells	
Quantitative analysis	
Volatile electrolytes	
Fast Response	
Versatility	
Condensable gases	

Summary

The DEMS/OEMS options detailed in this TI sheet are user interchangeable. The options available illustrate the versatility of the Hiden HPR-40 DEMS mass spectrometer system for DEMS/OEMS and other real time gas/vapour analysis applications.

In addition to the many applications in electrochemistry illustrated in this TI sheet, sample inlets are available for MIMS, TG-MS and other applications where real time analysis of gases and vapours is required.

References

1. Ashton S J (2012), Design, Construction and Research Application of a Differential Electrochemical Mass Spectrometer (DEMS), Springer Theses

2. Clark, Ezra L., et al. (2015) Differential electrochemical mass spectrometer cell design for online quantification of products produced during electrochemical reduction of CO2. Analytical chemistry 87.15: 8013-8020.

3. Ezra L. Clark, and Alexis T. Bell (2018), Direct Observation of the Local Reaction Environment during the Electrochemical Reduction of CO2. Journal of American Chemical Society 140 *(*22), 7012-7020

4. Z. Peng at al. (2012) A Reversible and Higher-Rate Li-O_2 Battery, Science, Vol. 337 no. 6094 pp. 563-566