

Gas Analysis | DEMS

Technical Information TI-20022.3

Summary of DEMS / OEMS Options

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

Measurement of dissolved gases is typically performed using a PTFE membrane which allows dissolved and entrained 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 and accessory to DEMS and OEMS applications.

DEMS: Measurement of Dissolved and Entrained Gas in Aqueous Electrolyte

ECL-Static

This DEMS thin layer cell design is 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].

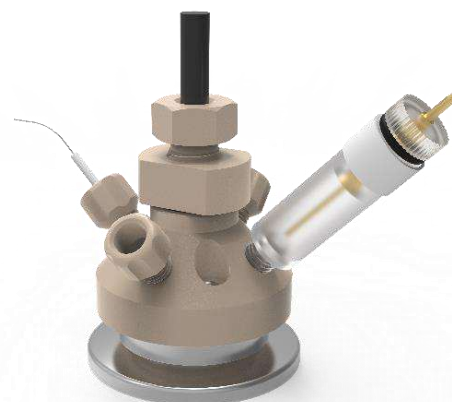


Figure 1: Assembled ECL-Static

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 10 $\mu\text{l/s}$.

The cell includes a 5mm diameter vitreous carbon working electrode which is suitable either as inert electrode or for a variety of deposition techniques.

A platinum wire counter electrode is also supplied to ensure optimum surface area.

The 'research ready' three electrode setup is completed with Ag/AgCl reference electrode.

ECL-Static electrode view

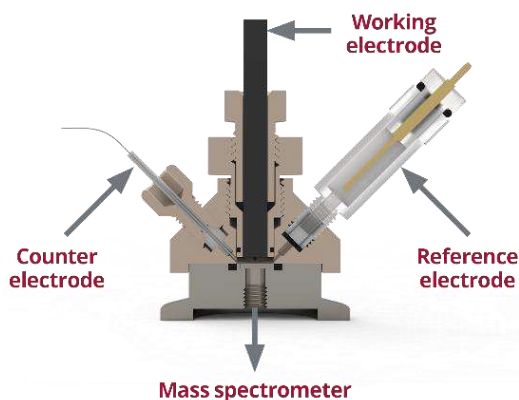


Figure 2: Electrode Configuration of ECL-Static

The cell features four 1/4"-28 UNF ports suitable for adaptation to custom counter and reference electrodes as well as inlet and outlet flow, through 1/16" fittings.

ECL-Static electrolyte view

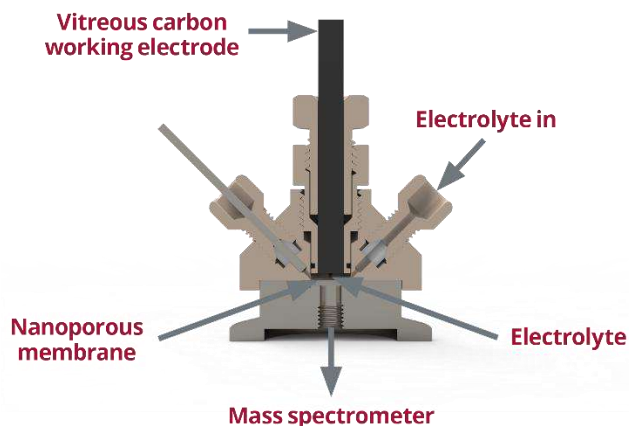


Figure 3: Port Configuration of ECL-Static

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	
Electrodeposition	
Ink deposition	

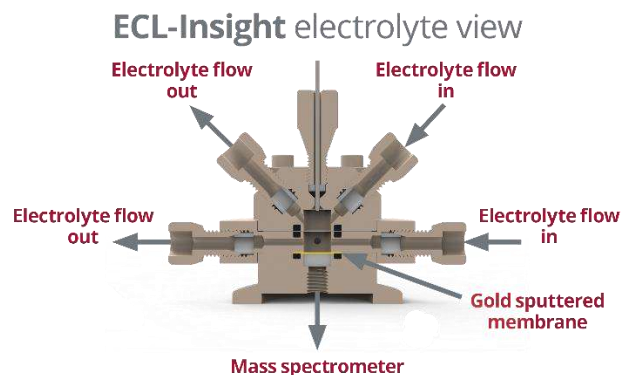


Figure 6: Flow Configuration of ECL-Insight

Port connectors are 1/4"-28 UNF with 1/8" hole so are suitable for increased flow and connection of custom reference electrodes.

The Insight cell also uses a PEEK body and PTFE membrane so is suitable for corrosive electrolytes.

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

ECL-Probe

The ECL-Probe allows dissolved gas to be measured in custom cells. The probe body is 6 mm diameter with connection to the MS via a 1/16" tube. The probe or the tube can be used to secure the probe into a cell. The 1/16" tube is detachable so can be cut to optimise for fast response or extended to integrate into the electrochemical workstation.



Figure 7: ECL-Probe

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 µm) is used to achieve the optimum MS sampling pressure for maximum sensitivity and fast response time.

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

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

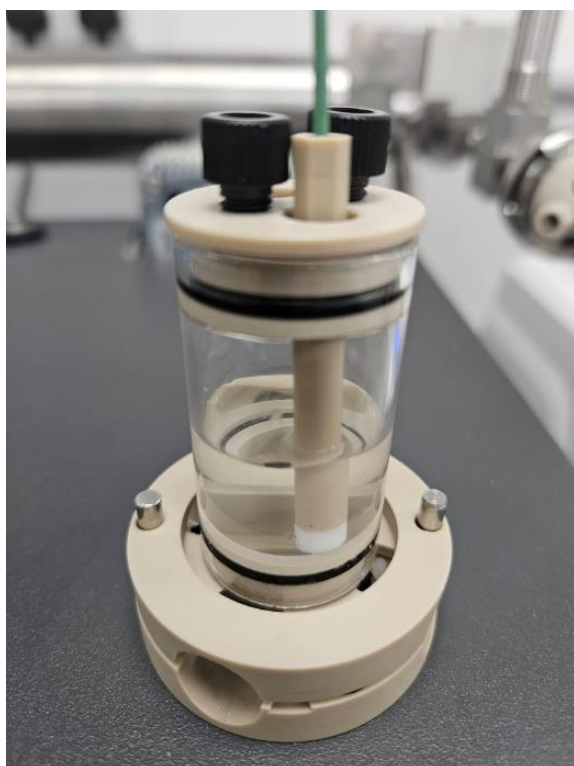


Figure 6: ECL-Probe fitted inside Redox.me cell

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	

OEMS: Measurement of Evolved Gas

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 200 $\mu\text{l}/\text{min}$, flow is similar to that recommended for use with the ECC-DEMS cell from EL-Cell [3] but is also suitable for connection to Redox.me or a custom cell.



Figure 7: 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 (<1 ml/min) of carrier gas to flow to the inlet of the cell, with a T piece at the outlet for capillary connection and exhaust. This ensures minimal dilution of product gas by carrier gas whilst ensuring capillary consumption is satisfied.

The 1/16" end fitting connects to the PAT cell quick connects, allowing for oxygen free cell loading and subsequent analysis, outside of an Argon box.

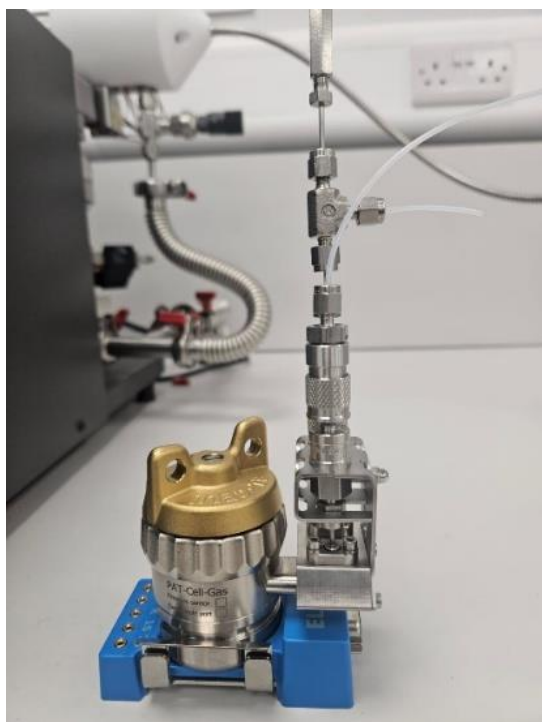


Figure 8: ULF connection to a PAT cell, with quick connects

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 9: 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 25 $\mu\text{l}/\text{min}$, 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 (25 $\mu\text{l}/\text{min}$) or 2 m (12 $\mu\text{l}/\text{min}$), 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.

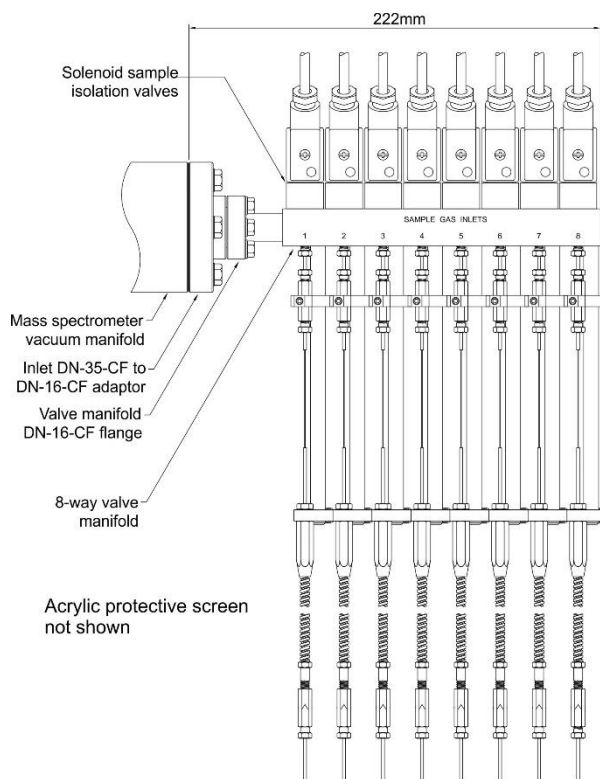


Figure 10: 8 Stream option for Microflow capillary

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 800 μ l to 28 ml/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 Hiden HPR-40 DEMS and HPR-20 OEMS offer a versatile range of user configurable inlets and accessories that can be used for many applications in electrochemistry studies.

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. 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
3. Z. Peng et al. (2012) A Reversible and Higher-Rate Li-O₂ Battery, Science, Vol. 337 no. 6094 pp. 563-566