

Chapter 2

Differential Electrochemical Mass Spectrometry

The intention of this chapter is to provide an overview of the DEMS technique, the instrument designs and example research applications. This involves the presentation and discussion of previous design solutions, which are separated into three parts: the electrochemical cell, membrane interface and the vacuum system of the mass spectrometer. Example experiments from the DEMS literature are then briefly described which highlight where a particular DEMS electrochemical cell design may be favoured. Ultimately, the appropriate design solution is determined by the intended research application of the DEMS instrument.

2.1 Principle of Operation

Differential Electrochemical Mass Spectrometry (DEMS) is essentially an analytical technique that combines electrochemical half-cell experimentation with mass spectrometry. This allows the in situ, mass resolved observation of gaseous or volatile electrochemical reactants, reaction intermediates and/or products. By correlating the faradaic electrode current with relevant mass ion currents, ambiguous electrochemical reaction processes can be elucidated, whereas standard electrochemical techniques such as the RDE are otherwise limited to the interpretation of a single electrode current. An overview of the DEMS instrument is depicted in Fig. 2.1.

The instrument essentially consists of three crucial components: an electrochemical half-cell, a PTFE membrane interface, and a vacuum system including the quadrupole mass spectrometer (QMS). The role of the electrochemical half-cell is to enable controlled electrochemical experimentation at a WE of interest, and to allow reaction products to be transported to the membrane interface. This interface consists of a microporous PTFE membrane that partitions the aqueous electrolyte of the electrochemical cell from the high vacuum conditions required

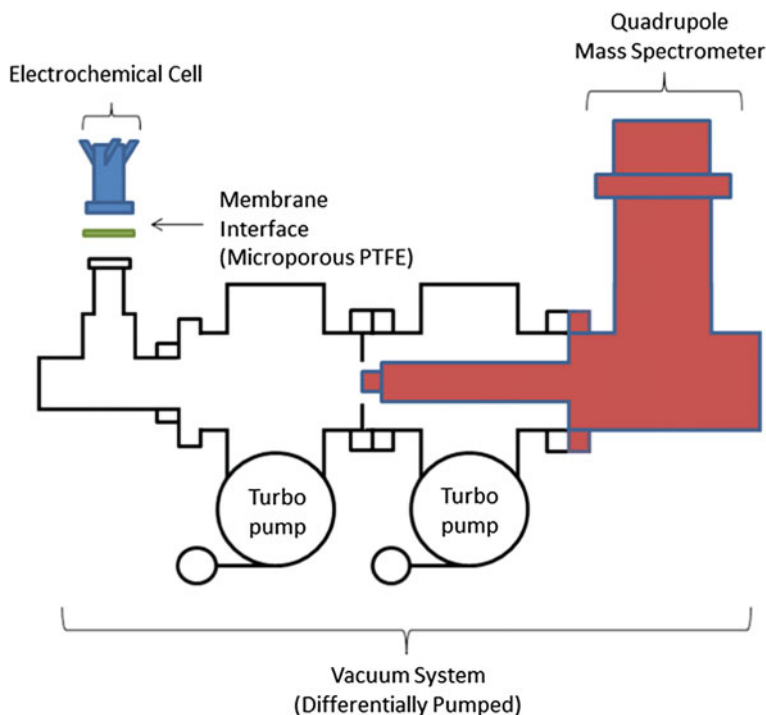


Fig. 2.1 An illustration of the typical components of a DEMS instrument. The DEMS instrument consists of an electrochemical cell that is interfaced to a (2-stage) differentially pumped vacuum system containing a QMS via a microporous PTFE membrane interface

by the QMS. The hydrophobic nature of the membrane prevents the passage of aqueous electrolyte, whilst allowing dissolved gaseous, volatile and relatively non-polar species to permeate, evaporating into the vacuum system. The permeating species may be subsequently observed online by monitoring the relevant mass ion current with QMS. The operation of the QMS, however, requires high vacuum conditions and consequently a specially designed, differentially pumped vacuum system is typically necessary.

The DEMS technique was first established by Wolter and Heitbaum in 1984 [1], however, the origins of utilising mass spectrometry to study electrochemical processes via a PTFE interface may be traced back further to Gadde and Bruckenstein in 1971 [2]. The ‘differential’ term was chosen in order to distinguish between the time- and potential- resolved correlation of the mass ion and electrode current technique [1] from un-resolved integrating methods [2, 3]. The study of dissolved gases in aqueous solution using mass spectrometry via a membrane interface, however, maybe traced back even further to Hoch and Kok in 1962 [4]. Because DEMS incorporates a membrane interface, the technique is closely related to the analytical technique referred to as membrane introduction mass

spectrometry (MIMS). Essentially, the only features that distinguish DEMS from MIMS are the incorporation of an electrochemical half-cell, and the exclusive use of a PTFE microporous membrane interface in DEMS. Despite the almost 30 year history of DEMS, however, no commercial instrument is available and as a result DEMS has been largely limited to the academic research environment where it has been used in a range of fundamental research studies on a variety of different electrodes, albeit by a relatively small number of research groups. Consequently, a number of DEMS design solutions have appeared in the literature over the years, with particular variations in the electrochemical cell design.

2.2 Instrument Design Solutions

The following section is intended to briefly introduce, discuss and evaluate the varieties of DEMS electrochemical cells, membrane interfaces and vacuum system designs that are present in the scientific literature.

2.2.1 *Electrochemical Cells*

The most flexible aspect of the DEMS instrument is the electrochemical cell design. A number of different DEMS cell designs have gradually evolved over the past 25 or so years, each tailored towards the study of different electrochemical reactions on various types and size of electrodes, ranging from porous [5] or smooth model electrodes [6] to HSAC precious metal catalysts [7] and even fuel cell MEAs [8]. Some of the more noteworthy cell designs will be presented in this section, along with a discussion of their respective advantages and limitations.

2.2.1.1 The Classic Cell

The DEMS technique was first demonstrated using the ‘classic’ DEMS cell [1]. The most defining feature of this cell is the porous membrane electrode whereby powdered electrode material is deposited directly onto the PTFE membrane interface to form the WE. An illustration of the classic DEMS cell construction is given in Fig. 2.2.

The classic DEMS cell construction consists of a modified vacuum flange containing a stainless steel frit that mechanically supports the porous membrane WE. The membrane electrodes were originally prepared by painting a lacquer containing small metallic particles (e.g. Pt) directly onto the PTFE membrane [9]; however, this was soon adapted so that an electrocatalyst layer could be sputter deposited directly onto the PTFE membrane interface [5], presumably to provide a more homogeneous layer. The electrochemical cell and membrane electrode are

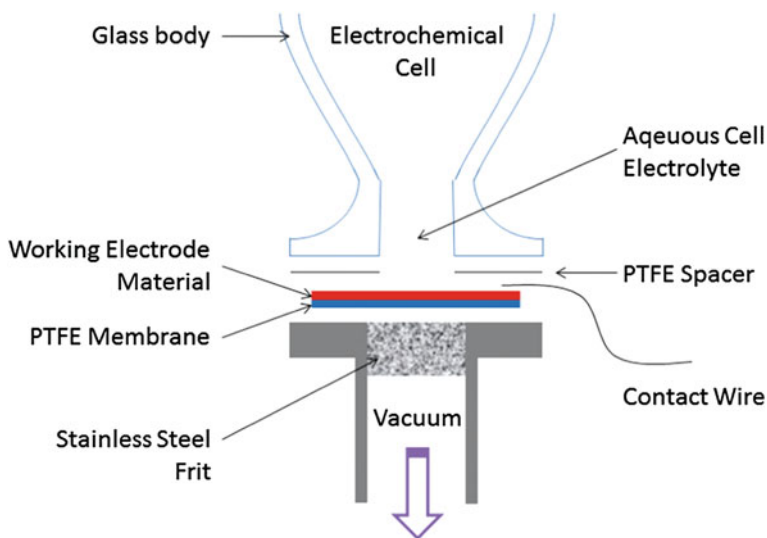


Fig. 2.2 An illustration of the ‘classic’ DEMS cell construction. The WE material is deposited directly onto the microporous PTFE membrane interface. The CE and RE (not shown) are then positioned in the electrolyte above the membrane WE

sealed between the vacuum flange and a PTFE ring which is compressed by the body of the electrochemical cell compartment. The electrochemical cell body has been typically constructed of glass although a PTFE cell has also been demonstrated [10]. Electrical contact to the WE meanwhile is achieved using a platinum wire, and the CE and RE are typically located within the single electrochemical cell compartment, positioned above the porous membrane WE via the multiple connections situated in the cell hood. These connections also serve to allow electrolyte to be deaerated, whilst also allowing electrolyte to be pumped through the cell if desired.

The principle advantage of this classic DEMS cell design is a fast mass spectrometry response time, typically <0.1 s and high collection efficiency of ca. 0.5 for lacquer and 0.9 for sputtered electrode [9]. Both are a consequence of the microscopic transport distances between the electrode surface and the vacuum side of the membrane. The cell may also be optimised to possess a small volume (ca. 1 to 2 ml) with static electrolyte, allowing very economical use of costly isotope labelled reactants for studies of electrochemical mechanisms [9]. The extremely close proximity of electrode material to the membrane interface does, however, introduce certain experimental difficulties. For instance, when using volatile reactants that readily evaporate through the membrane, their concentration at the electrode surface can be significantly reduced compared to the bulk, even with electrolyte convection. The competing process of evaporation through the membrane and adsorption of reactants onto the electrode surface could also lead to a

shift in reaction equilibrium [9]. Moreover, whilst convection of electrolyte over the WE may be achieved by positioning the cell electrolyte inlet hosing close to the membrane electrode (perhaps to some extent analogous to a wall-jet configuration), the true mass transport of reactants is very likely to be difficult to define and control. This is problematic when studying either steady state or diffusion limited processes, although an adaptation of the classic cell design incorporating a rotating rod to induce convection did appear to resolve this issue [11]. The design is further limited to experimentation with materials that can be deposited onto the PTFE membrane interface i.e. it is therefore impossible to, for example, study technical or smooth bulk electrodes such as single crystal or even polycrystalline electrode surfaces. Furthermore, the characterisation of WE material sample loading or utilisation and homogeneity (which is crucial in electrocatalysis) on the non-conducting membrane is difficult to quantify. Finally, the RE is also positioned within the electrochemical cell which can introduce impurities that can have dramatic consequences on the electrochemistry observed [12].

The trends in electrocatalyst research since the early inception of DEMS led focus away from powdered electrode materials that the classic DEMS cell was originally designed for, to more model systems such as polycrystalline and single crystal electrodes. As a consequence of these limitations, few new research studies utilising this DEMS cell alone have appeared for the past 15 years (with the exceptions of Ref. [13, 14]) and hence its designation in this review as the ‘classic’ DEMS cell.

2.2.1.2 Thin-Layer Cell

The thin-layer design first appeared in 1990 and was initially developed to allow the DEMS study of smooth bulk electrodes i.e. polycrystalline or single crystal electrodes [15]. The DEMS thin-layer flow cell construction illustrated in Fig. 2.3.

In contrast to the classic DEMS cell, the WE is now separated from the membrane interface via a thin-layer of electrolyte allowing considerably more flexibility in terms of the type of electrode that may be studied. Due to the miniaturised nature of this cell design ($\sim 1 \mu\text{L}$ volume [15]), the CE and RE are now placed in separate compartments, whose capillaries (which can be connected to either the electrolyte inlet or outlet) lead to the thin-layer WE compartment. However, the electrochemical reaction products must now diffuse from the electrode surface and across the thin layer before it may evaporate through the membrane to be detected by the QMS.

The obvious advantage of this design is improved versatility because a variety of well-characterised, bulk model WEs may be studied, and the preparation of a porous membrane electrode is no longer necessary. Furthermore, the flow of electrolyte and reactants over the electrode may be defined more exactly and easily controlled compared to the classic DEMS cell. The separation of the WE from the membrane interface, however, results in inherently longer delay times ca. 2–3 s [9, 15], although the collection efficiency is rather high ~ 0.9 [9] under static

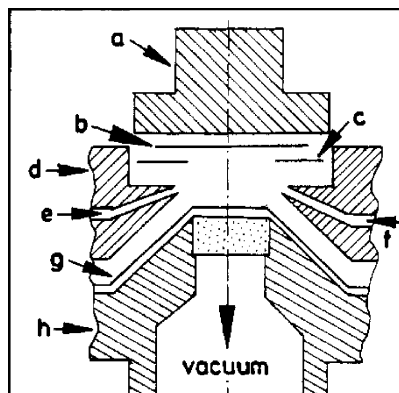


Fig. 2.3 A sketch of the thin-layer flow cell (a) electrode support, (b) platinum sheet (WE), (c) circular PTFE spacer, (d) cell body, (e) electrolyte outlet and connection to counter electrode, (f) electrolyte inlet, (g) porous PTFE membrane separating electrolyte and vacuum (support by a porous steel frit), (h) connection to vacuum chamber. Not shown, reference electrode connected by a third capillary. The WE in this cell design is separated from the membrane interface via a thin-layer of electrolyte allowing technical WE(s) to be used in DEMS. Reprinted with permission from Ref. [15]. Copyright 1990 American Chemical Society

electrolyte conditions. Under continuous electrolyte flow conditions efficiencies of only 0.2 or below are observed at practical flow rates of at least $1 \mu\text{l s}^{-1}$ [15]. Whilst the thin-layer cell can still be utilised to determine product formation rates under electrolyte flow conditions, there are a number of serious drawbacks. Firstly, the diffusion of reaction products across the thin layer is competing with the flow of electrolyte through the cell and therefore, any reaction products formed at the electrode close to the cell outlet may not be able to diffuse to the membrane before exiting the cell; the result of which is reduced collection efficiency. A second issue, regarding volatile and gaseous reactants is that these will, in addition to reacting at the WE, also evaporate through the membrane leading to a significant decrease in the concentration gradient along the cell flow field. This DEMS thin-layer cell design is therefore more appropriate for the study of desorption products under static electrolyte flow conditions [16–18]. As a consequence of the relatively poor cell collection efficiency during electrolyte flow conditions, in cases where convection of the WE is desired, the dual thin-layer flow cell is usually preferred.

Overall, the thin-layer cell is an ideal approach to the study of a variety of technical WE under static electrolyte conditions such as stripping or desorption measurements. However, in much electrochemical experimentation it is desirable to have a controlled and continuous flow of electrolyte and reactants over the WE surface for which the thin-layer cell is less appropriate.

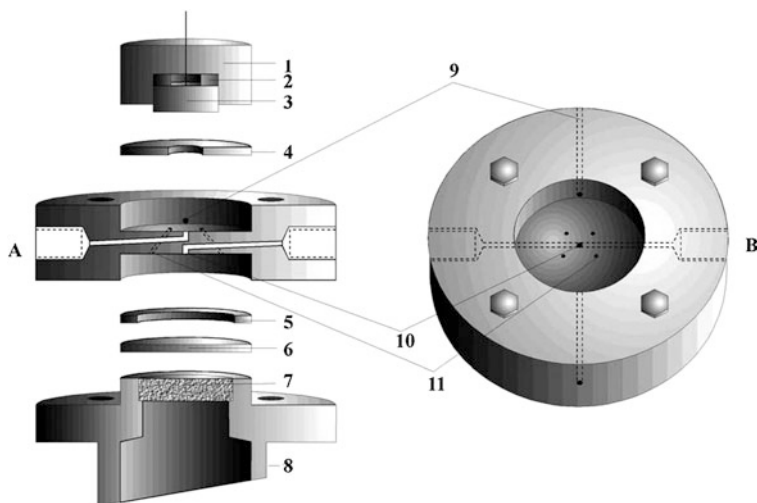


Fig. 2.4 A drawing of the dual thin-layer flow cell (1) Kel-F support, (2) Kalrez, (3) electrode, (4, 5) Teflon spacer, (6) porous Teflon membrane, (7) stainless steel frit, (8) stainless steel connection to MS, (9) capillaries for flushing with Ar, (10) inlet–outlet capillaries, (11) connecting capillaries. (a) Cross-section and top-view (b) of Kel-F cell body. The separation of the WE and membrane interface into two separate compartments avoid the problems associated with the original thin-layer design during the study of electrochemical reactions under electrolyte flow conditions. Reproduced by permission of ECS—The Electrochemical Society [3]

2.2.1.3 Dual Thin-Layer Flow Cell

A large quantity of the research performed in the past 10 years using DEMS has employed the dual thin-layer flow cell, depicted in Fig. 2.4.

The cell was initially developed to incorporate an electrochemical quartz crystal microbalance (EQCM), for combined DEMS and EQCM studies [3] but has since then, also been used to combine DEMS with attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR) [19, 20]. In contrast to the thin-layer flow cell described previously, the WE and membrane are now divided into two separate thin-layer compartments: a WE compartment and a membrane interface sampling compartment. As a result, two key problems associated with the thin-layer DEMS cell are avoided: firstly, the bulk concentration of gaseous and volatile reactants at the WE are no longer depleted by evaporation through the membrane, and secondly the cell collection efficiency is enhanced to ~ 0.4 under electrolyte flow conditions [9]. This is a consequence of the increased retention time of the electrolyte over the membrane interface. The dual thin layer cell has been typically constructed with either passivated titanium or PCTFE (Kel-f).

The dual-thin layer cell design is better suited to the monitoring of continuous faradic reactions, with controlled hydrodynamics in the determination of reaction product formation rates and turn over frequencies. A drawback of the dual thin-

layer flow cell, however, is a comparably slow response time, often ca. 2 s [21] or more because of the finite time required for the reaction products to be transported from the WE to the sampling compartment. Furthermore, the flow of electrolyte over the WE surface is not uniform and static regions exist making this particular cell difficult to compare to common hydrodynamic cells [22]. Finally, the thin-layers and capillaries linking the CE and WE to the RE are also of high resistance, which can introduce WE potential control issues, and the DEMS setup has required a modified 3-electrode electrochemical half-cell setup which incorporates two CE coupled via an external resistor [21, 23, 24].

The advantage of the dual thin-layer flow cell design is its ability to allow the study of continuous faradaic reactions under electrolyte flow conditions, avoiding the limitations of the thin-layer cell, namely the depletion of electrochemical reactants through the membrane interface and poor collection efficiency under flow conditions.

2.2.1.4 Capillary Inlet

An alternative approach to positioning the WE close to the membrane interface, is to position a PTFE membrane covered capillary inlet vacuum interface close to WE [25–28]. The capillary inlet (also known as the pinhole inlet) DEMS technique is illustrated in Fig. 2.5.

The inlet consists of a capillary whose tip is covered by [25], or imbedded with [26] a microporous PTFE membrane material. The capillary, for example, consists of a 0.6 mm diameter glass tubing with a 0.3 mm inlet diameter which is positioned between 10 and 20 μm away from the electrode surface [26]. Electrochemical reaction products which are formed close to the capillary inlet may then be either sampled by the membrane interface or simply diffuse away into the electrolyte bulk. The quantity of electrochemical reaction species entering the vacuum system is, therefore, inherently smaller than the regular membrane interface. The use of a capillary inlet was also extended in the multi-electrode scanning DEMS (SDEMS) cell allowing localised monitoring of reaction products over an electrode array [27, 28]. In this case the capillary inlet is attached to a three-dimensional piezoelectric-driven positioning system so that it may be moved along the length of a band of electrodes of different type or composition for catalyst screening. Here the capillary inlet consisted of a PTFE capillary tube, 0.15 mm in diameter with 20 nm pore Gore-Tex membrane, and was typically positioned 100 μm away from electrode [27].

The advantages of the capillary inlet system is essentially that DEMS can be used in combination with single crystal electrodes in the hanging meniscus configuration [25, 26] whereas the SDEMS system allows either a large number of electrode samples to be screened within a single experiment, or a particularly large electrode surface to be spatially mapped [27, 28]. The use of a rather small membrane surface area and capillary inlet also offers some advantages in terms of the DEMS vacuum system, which can be of a simpler design because of the

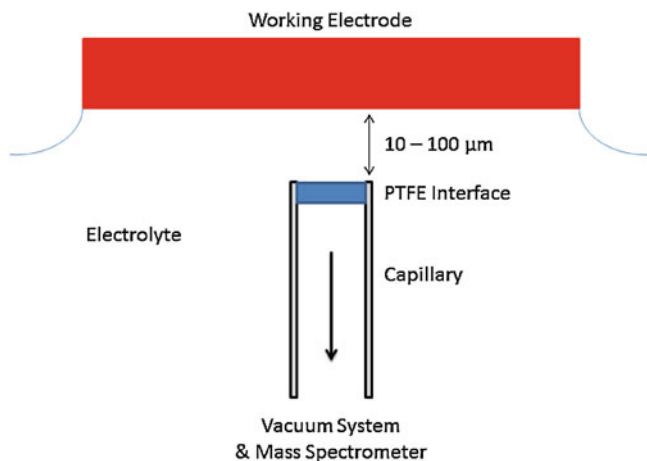


Fig. 2.5 An illustration of the capillary inlet DEMS electrochemical cell. The microporous PTFE membrane is incorporated into the end of a capillary whose interface is then positioned closely to the WE surface. This allows the study of either (1) single-crystal electrodes in a hanging meniscus configuration, or (2) multiple electrode arrays

inherently lower gas flux passing through the capillary (compared to the membrane of other cells), as will be discussed later in [Sect. 2.2.3](#). There are, however, a number of serious limitations. For instance, only a small fraction of the electrochemical reaction product is sampled resulting in an inherently lower instrument sensitivity. Furthermore, the capillary inlet interface samples from a larger volume than the cylindrical volume between the capillary inlet and electrode surface, and the amount of electrochemical reactants that enter the membrane capillary is sensitive to the capillary inlet position relative to the electrode surface. This perhaps makes calibration and quantitative experimentation somewhat tricky. The superposition of the products planar diffusion away from the surface and the spherical diffusion to the capillary may also lead to complicated time dependence and longer response times [9]. Finally, the capillary inlet would be inappropriate for experimentation requiring convection over the electrode surface.

2.2.2 Membrane Interfaces

In DEMS a microporous PTFE membrane is used to interface the aqueous electrolyte of the electrochemical cell with the high vacuum required by the mass spectrometer. The membrane acts as a selective barrier, preventing the passage of aqueous electrolyte into the vacuum system whilst allowing electrochemical reaction species to evaporate through into the vacuum to be detected by the mass

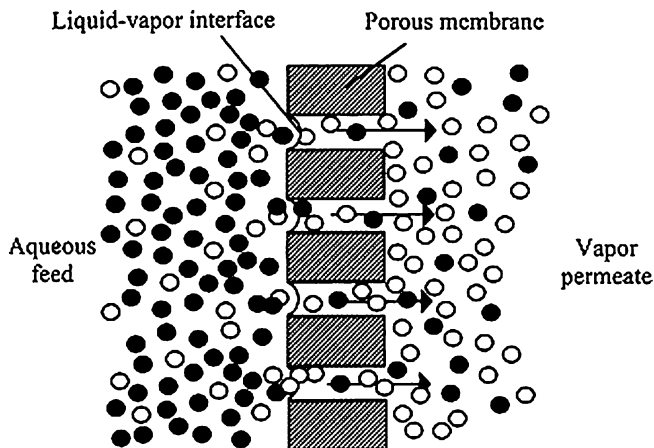


Fig. 2.6 An illustration of the vacuum membrane distillation process through a microporous PTFE membrane. The hydrophobic and microporous nature of the membrane interface prevents the passage of liquid electrolyte whilst allowing dissolved gaseous and/or volatile species to readily evaporate through the membrane pores. Reprinted from Ref. [29], Copyright 2001, with permission from Elsevier

spectrometer. The process is analogous to vacuum membrane distillation, a process which is depicted in Fig. 2.6.

The hydrophobic properties of the membrane prevent the penetration of the aqueous solution into the pores, resulting in a vapour-liquid interface at each pore entrance. The passive transport of species through the membrane pores is via the vapour phase and is instigated by the pressure drop across the membrane between the hydrostatic pressure of the aqueous electrolyte and the vacuum system of the mass spectrometer. The prevention of liquid transport through the hydrophobic PTFE membrane is rather dependent on a critical parameter, specifically the membrane pore size. For aqueous liquid the hydrophobic membrane must possess a critical pore radius of $< 0.8 \mu\text{m}$ in order to prevent liquid phase transport through the membrane [1]. This is a value determined by the Kelvin law and is dependent on the surface tension of the liquid, the contact angle between the liquid and membrane, and the applied pressure. For a given pore size, therefore, a critical hydrostatic penetration pressure exists above which the liquid phase will be transported through the membrane. Hydrophobic membranes with a narrow pore size distribution and high level of porosity are therefore preferred for this application [30]. The membrane specifications found in the DEMS literature, when provided, are summarised in Table 2.1.

In practice, the PTFE microporous membranes generally used in DEMS are typically $\sim 0.02 \mu\text{m}$ in size with a thickness between 50 and 110 μm . By using even smaller membrane pore sizes molecular flow in the pores is ensured, and the influence of isotropic effects during the gas transport are avoided [1, 38]. Almost all studies using DEMS have been performed in aqueous electrolyte with the

Table 2.1 Details of the DEMS microporous PTFE membrane interface specifications contained in the scientific literature

Pore size/ μm	Thickness/ μm	Porosity/%	Supplier	Geometric Area/ cm^2	Literature Source
0.2	60	50	Scimat	–	[7, 19, 21, 31, 32]
0.17	60	50		–	[33–35]
0.02	110	–	Schleicher & Schuell	–	[8, 36]
0.02	50	–	–	1.13	[3]
0.02	75	50	Gore	0.39	[34, 37]

In general the pore dimensions are $\leq 0.2 \mu\text{m}$ with thicknesses $\leq 110 \mu\text{m}$

exception being studies in organic electrolytes such as propylcarbonate (PC), dimethylsulfoxide (DMSO) [39] and dimethylcarbonate [13] which prove to be non-wetting to the DEMS microporous PTFE membranes. There are of course also other membrane materials which may be suited to DEMS such as polypropylene and polyvinylidene fluoride (PVDF), although these are unlikely to possess any advantages in consideration of the superior durability, and chemical resistance of PTFE. Microporous PTFE membranes, meanwhile, are generally widely available in flat and capillary forms which can be unsupported; however, the PTFE membrane is more commonly laminated onto a nonwoven polypropylene support web to improve mechanical strength and handling.

The use of a PTFE microporous membrane does impose certain limitations on the type of species that may be detected using DEMS. In order for a species to readily evaporate through a PTFE membrane, it must be either gaseous or volatile, and relatively non-polar [9]. Although the closely related MIMS technique may employ a wide variety of membrane material, DEMS has so far exclusively used a microporous PTFE membrane interface because of a number of its properties, namely its robust and reliable hydrophobic character, mechanical stability, durability and chemical resistance in the electrochemical environment.

Despite the non-wetting properties of the PTFE microporous membrane, a significant quantity of aqueous electrolyte is still able to evaporate through the membrane pores and into the vacuum system owing to the significant pressure gradient across the membrane. It is therefore crucial that a reasonably sized vacuum system can sufficiently pump the continuous flux of gas penetrating the membrane and achieve the operating pressures required by the QMS. This parameter, however, is not a typical specification of PTFE membranes which are for instance, more commonly employed for filtration in HPLC or woven into high performance clothing. There are some literature values for the total gas flux value of a PTFE membrane, which was calculated to be $0.09 \text{ mbar l s}^{-1}$ at 20°C assuming a water vapour pressure of 23 mbar, and $0.4 \text{ mbar l s}^{-1}$ at elevated temperature of 40°C [9]. Values other than these are rather scarce, and presumably depend on the exact specifications of the membrane i.e. pore size and thickness.

Finally, a membrane is not the only method of interfacing an electrochemical cell with a mass spectrometer. For example, a capillary had been used to sample

the gas above a closed electrochemical cell [40] or thin-layer flow cells have been combined with electrospray mass spectrometry [41–43] and inductively coupled plasma atomic emission spectroscopy (ICP-AES) for trace metal analysis [44]. The techniques, however, do not offer the time and potential resolved capabilities of DEMS.

2.2.3 Vacuum Systems & Mass Spectrometer

Despite that the hydrophobicity and pore size of the microporous PTFE membrane prevents the transport of liquid water, a considerable quantity is still able to evaporate through the membrane pores into the vacuum system. Consequently, a steady flux of gas $\sim 0.09 \text{ mbar l s}^{-1} \text{ cm}^{-2}$ that largely consists of water vapour (in addition to gaseous, volatile and non-polar species) enters the vacuum system [9]. The requirement of the vacuum system is to therefore pump at such a rate, that the necessary operating pressure of the mass spectrometer is obtained, typically $<1.0 \text{ E}^{-5} \text{ mbar}$. The exact design of the vacuum system can have important implications on the performance of the DEMS instrument, both in terms of pumping efficiency and mass spectrometer sensitivity [21]. However, the details of the DEMS vacuum system such as the exact operating pressures or membrane gas flux are seldom presented or discussed in the literature, and the vacuum system is often simply described as being *differentially pumped*.

Differentially pumped vacuum systems are not specific to DEMS but are generally useful when requiring to measure trace constituents of gas at relatively high pressure, for example 1 mbar, using a mass spectrometer that must operate at $<10^{-5} \text{ mbar}$ vacuum pressure. The differentially pumped vacuum system essentially consists of two or more, individually pumped vacuum chambers that are connected by a small aperture or skimmer. To illustrate why a single vacuum system is not sufficient, we can consider a reasonably sized vacuum system with a pumping speed of 300 l s^{-1} which must operate at 10^{-5} mbar pressure. The total gas flux that can be pumped by this system is $3 \times 10^{-3} \text{ mbar l s}^{-1}$. In order to interface this vacuum system to an electrochemical cell via a microporous PTFE membrane with a total gas flux of $0.09 \text{ mbar l s}^{-1} \text{ cm}^{-2}$ then the acceptable membrane interface geometrical area is 0.033 cm^2 . Although a single pumping stage may be sufficient for the capillary inlet DEMS vacuum system [26], such a small membrane surface area is rather impractical for the classic and thin-layer DEMS cells, which employ somewhat larger geometrical areas $\sim 1 \text{ cm}^2$ [3, 15]. In order to allow a larger membrane interface geometric area and therefore gas flux, a differentially pumped vacuum system must be employed. By using a vacuum system with two chambers, and allowing a relatively high vacuum pressure of $\sim 10^{-3} \text{ mbar}$ in the first pumping chamber, with a pumping speed of ca. 90 l s^{-1} a total gas flux of $0.09 \text{ mbar l s}^{-1} \text{ cm}^{-2}$ can be pumped, allowing a more practical membrane geometric area of $\sim 1 \text{ cm}^2$. The pressure in the 2nd chamber, containing the QMS, therefore, may be determined by controlling the conductance

of gas between the 1st and 2nd pumping chamber using an aperture, in order to obtain the necessary operating pressure of the mass spectrometer $<10^{-5}$ mbar. For example, a 200 l s^{-1} pumping speed in the second chamber would allow an operating pressure of the mass spectrometer of 10^{-5} mbar to be achieved using an aperture with a conductance of $\sim 2 \text{ mbar l s}^{-1}$. A circular aperture with a radius of 0.85 cm would therefore be acceptable, and can be easily machined.

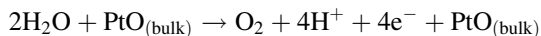
Previous DEMS instruments vacuum systems have employed a number of different types of pumps for the 1st chamber, such as a rotary vane pump [8, 45], diffusion pump [11], or turbo pump [9]; however, all instruments used a turbo pump for the second pumping stage containing the mass spectrometer. It has been claimed that a higher sensitivity of the DEMS achieved by positioning the ion source between the first and second DEMS chambers [21] although exact details are not given. This can presumably be attributed to allowing a higher pressure at the ion source, which increases the number of ions produced relative to the vacuum system background. Once a differentially pumped vacuum system has been constructed and can accept a certain gas flux, the vacuum system is not necessarily limited to DEMS, as highlighted in a previous instrument [45], whereby the DEMS vacuum system and QMS was used in combination with thermo-gravimetric analysis. For the related MIMS technique, however, differentially pumped vacuum systems are generally not required because total gas fluxes through the membranes are much smaller owing to the different non-porous membrane types used [34].

2.3 Research Applications

The purpose of this section is to briefly analyse the types of experiments that may be performed using DEMS, and highlight when certain DEMS electrochemical cells are favoured.

2.3.1 Radio-Isotope Labelled Experimentation

The very first DEMS study using radio-isotope labelled reactants was simply entitled ‘Does the oxide layer take part in the oxygen evolution reaction on Platinum’ [46] and aimed to elucidate whether or not the PtO layer formed on Pt electrode $>0.9 \text{ V}_{\text{RHE}}$ was involved in the oxygen evolution at potentials $>1.5 \text{ V}_{\text{RHE}}$ according to the following reaction:

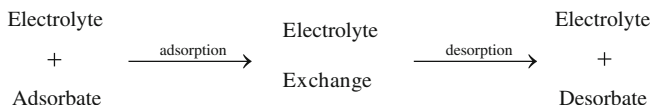


This study nicely demonstrates the power of DEMS using radio-isotope labelled reactants, employing the classic DEMS cell. Although Pt electrodes possess relatively poor activity toward the oxidation of water, it is considered to be a model

electrode useful for fundamental studies on the oxygen evolution reaction (OER) mechanism, and there was some debate concerning the role played by the Pt oxide layer. By using H_2^{18}O to form an oxide layer of Pt^{18}O species, the DEMS instrument could be used to observe whether the O_2 evolved during the oxidation of H_2^{16}O contained any $^{16}\text{O}^{18}\text{O}$ species in circumstances where the oxide layer does take part, or if only $^{16}\text{O}^{16}\text{O}$ species are formed. In this study, only $^{16}\text{O}^{16}\text{O}$ species were observed, indicating that the oxide is not consumed during the OER. In this case the classic DEMS cell was quite suitable because the experiment purely concerned the fundamental study of a surface reaction and does not require the use of more technical bulk electrodes, and that the cell could be optimised to possess a small volume using little of the expensive radioisotope labelled water.

2.3.2 Characterisation of Organic Adsorbates

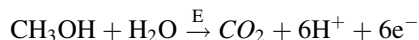
The first application of the thin-layer DEMS cell, which allowed the use of smooth electrodes by separating the WE from the membrane interface, was to study the cathodic desorption and hydrogenation of benzene to cyclohexane on an annealed Pt electrode, in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ [15]. The general procedure for this type of study is described by the following process:



These types of experiments involve adsorbing a certain reaction species, such as benzene at $0.5 \text{ V}_{\text{RHE}}$, which is saturated in the starting cell electrolyte. The electrolyte is then exchanged with the pure electrolyte removing the saturated species, whilst maintaining the WE potential at a fixed value. The WE potential is then swept to a potential where the pre-adsorbed species may desorb from the WE surface. In this study, it was observed that benzene partially desorbs without reaction in the $\text{H}_{\text{upd/ads}}$ potential region, however, at more negative potentials where the hydrogen evolution reaction takes place on Pt, the benzene is hydrogenated and desorbs in the form of cyclohexane [15]. In adsorption and then desorption measurement such as these, where no convection of the electrolyte is required during the electrochemical experimentation (except to exchange electrolytes), the thin-layer cell is very suitable and can incorporate almost all types of technical electrode. Finally, in addition to benzene there are numerous other desorption studies such as acetone [47], bicyclic aromatics [48, 49], ethene [6, 16] systems, each employing the thin-layer cell.

2.3.3 Study of the Electro-oxidation of Small Organic Compounds

One of the first ever DEMS studies focused its attention towards the study of the methanol oxidation reaction (MOR) which is of fundamental research interest for direct methanol fuel cell (DMFC) development [37]. Since then, the MOR [7, 21, 31, 50, 51] and other potential organic fuels that are oxidised to carbon dioxide, such as ethanol [32, 52–54] have been quite extensively studied using DEMS on a number of electrode systems. The overall MOR may be described by the following reaction formula:



However, it was long since suspected that the MOR does not reach completion based on strange dependences of the MOR current on the convection of electrolyte using conventional RDE techniques [55]. This assumption could, however, not be confirmed using standard RDE techniques alone because only a single faradaic electrode current is observed. In contrast, DEMS is able to monitor in situ both the consumption of methanol [56], and the generation of partially oxidised intermediates [57] and carbon dioxide [7, 21, 31, 50, 51] allowing the calculation of the MOR current efficiencies and study of the reaction mechanism. The dual thin-layer flow cell is particularly suitable for the study of the MOR under flow conditions owing to its advantages over the thin-layer flow cell during experiments using electrolyte convection i.e. there is less depletion of reactant in the electrolyte along the flow vector, and higher electrode collection efficiencies are achieved.

2.4 Conclusions

The intention of this chapter was to provide an overview of the literature concerning DEMS, with particular focus on previous design solutions and their respective advantages and limitations, prior to the design of the DEMS instrument to be constructed in this thesis. The DEMS instrument requires the custom design and fabrication of three parts: the electrochemical half-cell, membrane interface and vacuum system.

Various DEMS electrochemical cell designs have appeared over the years with varying degrees of success. In recent years, few publications have appeared using the classic DEMS electrochemical cell that deposited the electrode material directly onto the membrane interface, primarily because electrochemists today are rather more interested in the study of smooth electrode surfaces, which cannot be incorporated with the microporous PTFE membrane and must therefore be separated. The most implemented DEMS cell designs of the past 10 years or more, are the thin-layer, and in particular, the dual thin-layer electrochemical flow cells. In these designs the electrode and membrane are separated via either a thin-layer layer of

electrolyte, or by placing them in two separate thin-layer compartments. These cells allow the use of bulk electrodes with sufficient sensitivity, whereby the thin-layer cell is favoured under static electrolyte conditions, whilst the dual-thin layer cell is more suited to continuous flow experiments. In general, the requirements of the electrochemical cell is to incorporate the electrode and vacuum interface of choice, allow controlled electrochemical experimentation at the WE, transport electrochemical products to the vacuum interface and obtain sufficient time and potential resolution.

All DEMS design solutions employ a microporous PTFE membrane in order to interface the aqueous electrolyte of the electrochemical cell and the vacuum system of the mass spectrometer. The membrane permeation process is analogous to vacuum membrane distillation. In order to prevent the passage of liquid water, the radius of the membrane pores must be $<0.08\ \mu\text{m}$. The use of a PTFE membrane does, however, impose certain restrictions on the electrolytes that may be used, along with the electrochemical reaction species that can be detected, because only dissolved gaseous, volatile and relatively non-polar species readily pass through the microporous membrane. Despite the hydrophobic properties of the PTFE membrane, a considerable amount of water still evaporates into the vacuum system, often requiring a specifically designed differentially pumped vacuum system.

The requirement of the DEMS vacuum system is to pump away the gas flux that passes through the PTFE membrane at such a rate that the necessary vacuum conditions required for the mass spectrometer are maintained. In order for this to be achieved using both a sensibly sized vacuum system, and a reasonable membrane interface surface area (or gas flux), a two-stage differentially pumped vacuum system is often employed. Such vacuum systems are not specific to DEMS but are often used when a gas at relatively high pressure $\sim 1\ \text{bar}$ must be measured online using mass spectrometry. Details of the total gas flux through the PTFE membrane, vacuum system and corresponding operating pressures of a DEMS instrument are, however, rather scarce in the literature.

DEMS has been utilised to study a variety of electrochemical reactions on various electrode systems. For instance, the classic DEMS has been used in combination with radio-isotope electrochemical reactants to elucidate the origins of electrochemical surface species. The development of the thin-layer cell for DEMS allowed the study of smooth electrodes and is particularly suitable to the study of electrode adsorption potential induced desorption products which do not require convection. However, convection can be desirable for experiments involving continuous faradaic reactions, such as the electrochemical oxidation of small organic compounds. In such cases the dual thin-layer flow cell is preferred.

Overall, there is no commercially available DEMS instrument and the design of the custom parts must be tailored toward the intended research application of the instrument.

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Ashton, S.J.

2012, XX, 224 p., Hardcover

ISBN: 978-3-642-30549-8