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A Review of Differential Electrochemical Mass Spectroscopy TechniqueⅠ.The principle and development of DEMS

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差分电化学质谱方法(DEMS)的回顾

I. DEMS原理和发展

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摘要　差分电化学质谱(DEMS)是将电化学和质谱技术相结合而发展起来的一种现代电化学现场测试手段.它可现场检测电化学反应中的挥发性气体产物及动力学参数，中间体及其结构的性质等.当电极反应产物为共析出时，DEMS技术可同时确定每种产物的法拉第电流随电极电位或时间的变化.全文分两部分，第一部分回顾DEMS方法的原理与发展；第二部分介绍DEMS方法的应用.本文为其中之第一部分.

关键词　DEMS方法，质量电流，旋转电极引入系统，点接触引入系统

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A Review of Differential Electrochemical Mass Spectroscopy Technique I. The principle and development of DEMS①

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With the advance of electrochemistry, the modern electrochemistry techniques have played a very important role in the investigation of intermediates and products in electrochemical processes. These methods combined with electrochemistry include *in situ* or *ex-situ* spectroscopic analysis such as, Raman[1,2] or IR-spectroscopy[3], and surface analysis such as XPS[4,5] or Auger spectroscopy[6] as well as gas phase chromatography. Among versatile spectro-electrochemical methods[7,8], Differential Electrochemical Mass Spectroscopy (DEMS) has been found to be one of powerful analysis methods[9] in *in situ* detection of intermediate species, products and electrochemical kinetic properties during the electrochemical reactions.

Bruckenstein and co-workers first developed Electrochemical Mass Spectrometry (EMS) for the most definite *in situ* analysis of the volatile gaseous reaction products more than twenty years ago[10~13]. The hydrophobic porous electrode, which was fabricated by rubbing finely divided platinum into a little wetted fine glass frit and then teflonating, is sandwiched between the solution being electrolysed and the high-vacuum system of a mass spectrometer. The mass intensity detected after a response time of ca. 20s was directly proportional to the amount of a gas product. Anderson and co-workers proposed a similar setup using silicon rubber membranes in 1980[14]. But there was still an appreciable delay between the mass intensity and the amount of a product. Some years later, Wolter and Heitbaum[2,15] improved the method so that the time derivative of the amount of the species produced, i. e. the rate of

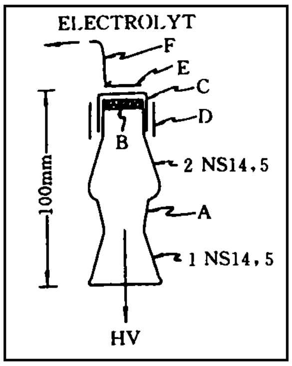

Fig. 1 Scheme of membrane system with working electrode
A, glass body; B, glass frit; C, thin porous teflon membrane; D, the membrance fixed with a teflon shrinking tube; E, working electrode; F, electrolyte

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formation, could be measured and called it Differential Electrochemical Mass Spectroscopy (DEMS). DMES method used a fine non-wetting microporous PTFE membrane as separator (Fig. 1) with a typical response time of ca. 0. 5~0. 2 s[2, 16]. So, its sensitivity was improved greatly, and the mass intensity detected was proportional to the corresponding electrochemical current. The DEMS method can offer the unique advantages of on-line detecting the volatile products during the electrochemical processes as a fuunction of the electrode potential or time, differing from gas chromatography as used in the ordinary studies. It can also measure the rate of formation of a product as well as its current efficiency under sweeping potential and thus give not only analytical but also kinetic information. In addition, structural information about the intermediate is gained when the isotope labelling is used[17]. In this review, we are going to introduce separatly the DEMS method and its improvements as well as some applications in electrochemical reactions.

1 DEMS Method

The detail of the principle of DEMS has been described in the literature[2]. Basically, the experimental set up is composed of three parts, namely the electrochemical and mass spectroscopic equipments and the membrane inlet system. A simple quadrupole instrument (Anelva AQA-200) can meet the needs of mass spectrometer used in DEMS. Most of the inlet systems consist of either conducting electrodes deposited on porous hydrophobic teflon membrances with a pore radius of ca. 0. 02 μm and a thickness of 75 μm or amalgamated metal-mesh electrodes pasted on the membrane[18]. The membrane is directly attached to the ionization chamber of a mass spectrometer. The volatile products are able to permeate into the membrane and reach the ion source of mass spectroscopic system by vacuum. Therefore, the mass signals of products are detected shortly after their formation, and in the meanwhile the ionization chamber is pumped continuously ($<10^{-3}$ Pa operation pressure). The measured mass intensity of a given species is proportional to its incoming flux, which is also proportional to its faradaic current. The mathematical statements are as follows:

$$M_i = K^0 J \qquad (1)$$

$$J = (1/nF) N A F_i \qquad (2)$$

$$M_i = K^* (1/n) A F_i \qquad (3)$$

where M_i is the mass intensity of a given species, J is the flux through the membrane into the ionization chamber (mol · s^{-1}), K^0 is the constant which includes all mass spectroscopic constants and settings (C · mol^{-1}), n is the number of electrons transferred for producing one product molecule, F is the Faraday constant (C · mol^{-1}), N is the collection efficiency (ratio of the number of molecules reaching the mass spectrometer to the number of molecules produced on the electrode), A is the current efficiency, F_i is the faradaic current and constant K^* includes all factor which are not specific for a given electrochemical process[19]. In general, the mass intensity significantly exceeds the background level at 10 μA, and then, a rate of formation of 5×10^{-11} mol · s^{-1} can still be measured, which illustrates a high sensitivity of the method[3]. Fig. 2 shows a typical DEMS result with a simultaneous cyclic voltammogram of the methanol oxidation on Pt in sulfuric acid with a sweep rate of 0.4 V · s^{-1}, although the oxidation current is hidden by the capacitive current.

It is necessary to determine the K^* in advance in order to evaluate n. The oxidation of CO to CO_2 at Pt electrode, where n value is known, often served as a calibration system for K^*. The steps of determination of K^* are as follows:

(1) The absorption of CO on the electrode is taken at the potential E_{ad} = 25 mV vs. NHE for about 5 min, and afterwards the rest of CO in solution is removed by Ar flushing.

(2) The adsorbed CO was oxidized by a potential sweep from E_{ad} to E_r = 900 mV.

(3) The current and the mass intensity of CO_2 are recorded simultaneously as shown in Fig. 3[19].

The oxidation charge Q_1 is defined as the hatched area with positive mark in the cyclic voltammogram together with the area under the $F_i \sim t$ curve. In addition, the integration of the $M_i(CO_2) \sim E$ curve represents Q_{Mi}. Then, eq. (3) can be written in the following formula,

$$Q_{Mi} = K^* (1/n) A Q_1 \qquad (4)$$

The number of electrons n can be determined from eq. (4), so that this result gives us the possibility of obtaining information about strongly adsorbed intermediates although they are not volatile or gaseous and thus cannot be detected directly by a mass spectrometer.

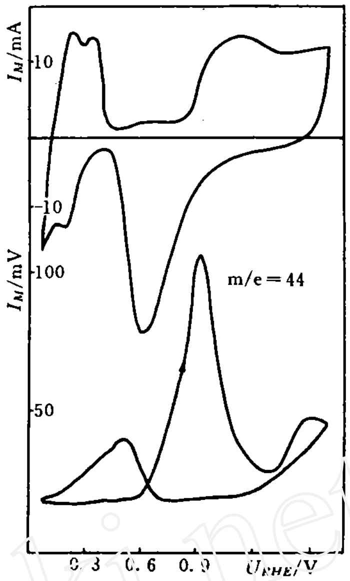

Fig. 2 The cyclic voltammogram I/V (above) and I_M/V curves of (below) at a porous Pt-electrode in 0.5 M H_2SO_4 + 2.5 × 10^{-3} CH_3OH (deaerated), sweep rate: 400 mV s^{-1}

2 Improvement of DEMS System

Since Heitbaum and his co-workers developed the DEMS method in the middle of 1980s, many research works have been done using an *in situ* DEMS. Wolter and Heitbaum[20] studied the adsorption of CO on a porous Pt-electrode in sulfuric acid by DEMS. The others, for example, oxidation of CH_3OH and HCOOH[21~23], reduction of CO_2[28] as well as O_2 evolution[24,25] have been also investigated.

Although DEMS developed by Heitbaum et al provided us information about volatile products, the oxidation states of the strongly bound species when the faradaic charge of its electrodesorption was correlated with the integration of the ion current of the product molecules detected in the mass spectrometer[26,29] as well as the structural information about the intermediates, there were still some disadvantages under some experimental conditions. One of them was the huge flow through the membrane to MS. For example, a strong gas evolution at the working electrode, particularly the formation of hydrogen during CO_2 electroreduction, can not work well with porous metal film electrodes[30], because a high background mass signal would appear at the ion source. Moreover, in the conventional DEMS apparatus with a stationary solution, when a volatile reactant such as CO_2 was dissolved in the electrolyte, the reactant in the vicinity of the electrode surface would be depleted by the following three consumption routes, 1) the electrochemical reaction, 2) evacuation into a vacuum chamber and 3) carrying away by other gases due to the electrolysis of water[31]. In addition, Bruckenstein's method in 1980s could only be used for determination of real current in the any special cause of the desorption applying a calibration technique[32].

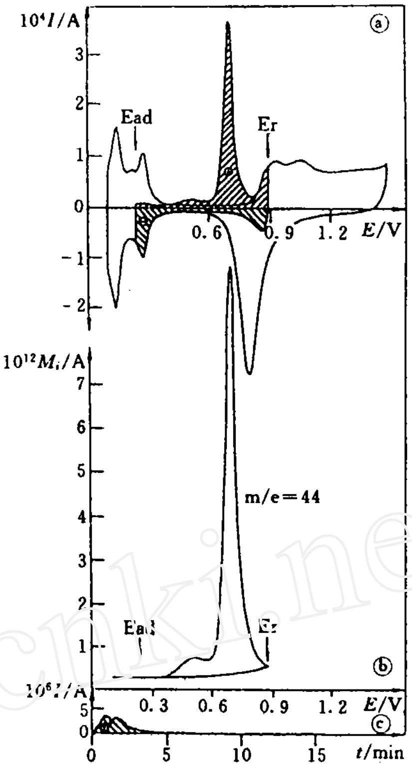

Fig. 3　K^* calibration. a) CV curve for CO adsorption and electrodesorption; b) $MI \sim E$ result for $M/e = 44$ (CO_2); c) current during the adsorption and Ar flushing. adsorption potential $E_{ad} = 225$ mV vs. RHE, reversal potential $E_r = 875$ mV, $dE/dt = 6.25$ mV s^{-1}, porous Pt electrode in 0.5 M H_2SO_4

2.1　On Line Rotating Electrode Inlet System and Mass Spectrometer

Nearly at the start of 1990s, to overcome these difficulties mentioned above, Tegtmeyer and Heitbaum, on the stimulation of the advantage of rotating disc electrode for electrochemical processes that diffusion limitation can be overcome by extrapolation to infinite rotation speed[33], combined the rotating disc technique directly with mass spectrometer[15]. A rotating inlet system was inserted between the mass spectrometer and the electrochemical cell in order to obtain well defined and calculable transport properties near the electrode. The porous metal electrode was directly deposited on the PTFE membrane and all volatile species were continuously evaporated into the mass spectrometer from the another side of membrane within several tenth of a second after their formation. In order to decrease a high background pressure of H_2O at the ion source, the extra pumping system was used. This method made the electrode behaviour a smooth one in the case of diffusion limited process. The collection efficiencies N in eq. (5)

$$I_i = K^0 (N/F) A (1/n) I_F \tag{5}$$

can be calculated from the slope of the diagram of I_i against I_f for different rotation speeds, where I is the ion current of a species at the detector and I_f is the faradaic current at the electrode. Therefore, the faradaic current of volatile product can be quantitatively correlated to the mass intensity. When more than one products are formed at the electrode, the true current potential curve for a given product can also be determined from its mass intensity concerning potentials. The authors in the paper[15] determined successfully the collection efficiency of H_2 evolution on the sputtered Pt electrode in 10^{-3} M $HClO_4 + 0.1M$ $NaClO_4$ solution.

As described above, porous metal film electrodes resulted in a considerable flow of gases into the ion source of mass spectrometer for the electrode reactions with strong gas evolution and strong background in mass spectrometer. Wasmus et al[30] constructed a new type of the cell as in Fig. 4. The working electrode in this case consists of a cylindrical rod of copper positioned closed to the PTFE (ca. 0.2 mm in thickness). When the cylinder electrode is rotated, a radical component of mass flow can be achieved and be transported towards the membrane and the ion source of the mass spectrometer. The rotation frequency would be responsible for the radial component of mass flow. The mass intensities of different *m/e* values for the different products are measured in time interval of 200 ms. This new DEMS method has been applied to study the electroreduction of CO_2 at different kinds of Cu electrodes in $KHCO_3$ solution by Wasmus and co-workers[30].

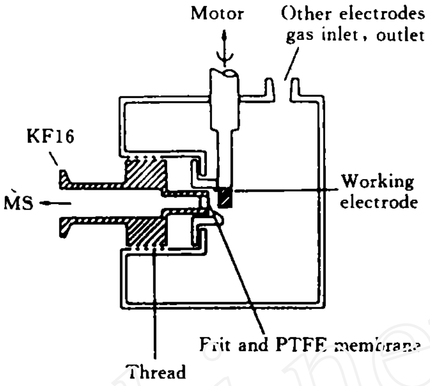

Fig. 4　Schematic diagram of the electrochemical cell for on-line mass spectroscopy of volatile products using a rotating cylinder electrode

It is an interesting idea for combining hydrodynamic voltammetric method with the DEMS technique. On the basis of works done by Heitbaum et al[15], Fujihira and co-workers[34] improved drastically the sensitivity of the quantitative analysis by setting up new hydrodynamic electrochemical cell as shown in Fig. 5. The stationary gas-permeable Au eledctrode sputtered on a non-wetting membrane was fitted in a rotational flow around the rotating rod, which promoted the mass transfer of reactants with forced convection of the electrolyte solution[31]. This new DEMS apparatus overcame the previous disadvantages on the complexity of the structure and the low collection efficiency. In addition, the another advantage of the new apparatus is that when the concomitant generation of more than two kinds of gases, like H_2 and CO, produces at the same electrode potentials, $I_{ms} \sim E$ curves give us definite answers to these questions, although it is difficult to know what kinds of gases evolve and what the composition of the evolved gases is only from the I-E curve for the previous DEMS. With the help of *in situ* DEMS technique[31], the $I_{ms} \sim E$ curve for CO during the reduction of CO_2 at Au in Na_2SO_4 solution became more obvious with an increase of the rotation speed.

2.2　'One Point Touth' Gases Inlet System

Kita and Gao have presented another new kind of gas inlet system in the literatures[35,36] as shown in Fig. 6. This system was called "one point touch" gases inlet system. The gas inlet has a pin-hole of a few micrometers in diameter located at the centre of the hemispherical end of a thick glass

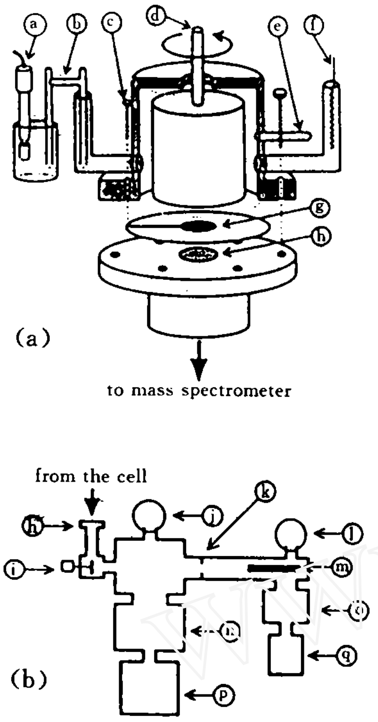

Fig. 5 DEMS apparatus with a rotating rod. a) The electrochemical cell and gas inlet system; b) the vacuum chamber and mass spectrometer. a, reference electrode SCE; b, liquid junction; c, current lead for the working electrode; d, rotating rod; e, gas bubbler; f, counter electrode; g, working electrode on the gas-permeable and non-wetting membrane; h, gas inlet; i, valve; j, ionization pressrue gauge; k, orifice; l, B-A type ionization pressure gauge; m, quadrupole mass spectrometer; n, main turbo molecular pump; o, sub-turbo molecular pump; p and q, oil rotary pumps

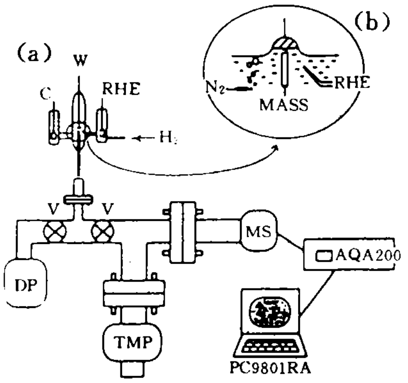

Fig. 6 New on-line mass specrometer with 'One point touch' gases inlet system. MS, mass detector and spectrometer; DP, diffusion pump; TMP, turbomolecular pump; C, counter-electrode; W, working electrode; V, valve; G, gas pipe. The inset shows the gas-inlet sytem

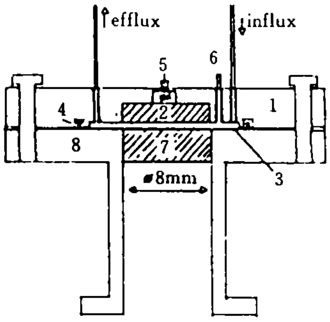

Fig. 7 Electrochemical thin-layer flow cell with membrane gas inlet system; 1, Kel-F cell; 2, glass frit; 3, working electrode; 4, viton-ring; 5, counter electrode; 6, metal lithium reference electrode; 7, steel frit; 8, KF-junction

tube of 4 mm in diameter. The pin-hole is covered with Teflon film of thickness of 50 μm. Gaseous reactants and products penetrate through the film and the pin-hole. Hence the effective area of the electrode for sampling is very small and the solution thickness between the electrode surface and the top of the gas inlet may be only a few micrometers. It has been used to investigate the electrooxidation of a monolayer of adsorbed CO and the electroreduction of dissolved acetylene at Pt single-crystal electrodes. This method is particularly suitable for electrochemical processes at a smooth or single crystal electrode and shows a high sensitivity even though the product is given only over a very small fraction of the electrode surface.

2. 3 Other Improvement of DEMS for Special Application

It is found that DEMS method has been applied successfully to aqueous solutions as well as widely-used organic solutions[37]. Hambitzer and co-workers constructed a new simplified DEMS experimental set-up, which could be used in a concentrated electrolyte solution, for example, inorganic electrolyte for a rechargeable Li/LiCoO_2 battery system[38]. The scheme in Fig. 7 is a combination of electrochemical thin-layer flow cell and membrane gas inlet system. The thin-layer flow cell filled with steadily flowing solution[39]in which the electrochemically generated species flow branching to the membrane-frit gas-inlet system. The time constant, often less then 0. 5s, relates to the volume of the connecting parts and the flow rate. Therefore, the better performance can be obtained by the combination of the two parts in one compact thin-layer cell. It is also used for the most electrochemical reactions occurring on the flat surface electrodes.

Skou and Munk[40] developed a simplified set-up for electrochemical mass spectrometry using silicon rubber membrane and a gold substrate. This silicon rubber membrane (ca. 25 μm in thickness) has a suitable time constant and sensitivity for the small molecules such as O_2, N_2, CH_4 and so on, which is comparable with those of the microporous PTFE membranes used generally. Furthermore, it eliminates the needs of a special prevacuum chamber and extra turbomolecular pump in the mass spectrometer. The gases, which transport in this kind of "tight" polymer membranes, are assumed to be dissolved in the membrane according to Henry's law, and then Fick's law gives the gases mass flow through the membrane. At last, the pressure in the ionization chamber itself is mormally below 10^{-5} Pa. usually, the response time for the spectrometer itself of the order of tens of milliseconds[2] and the dominant factors for the response time are the diffusion through the membrane (ca. 0. 12 s) and the flow through the interconnection (ca. 0. 5 s). An experimental result has been gained by the mass spectrometric cyclic voltammetry(MSCV) on the oxidation of methanol at platinum black in sulphuric acid.

3 Summary

The Differential Electrochemical Mass Spectroscopy (DEMS) technique has been developed rapidly,especially in the middle of 1980s and the earlier of 1990s, and brought into practical uses as one kind of powerful *in situ* detection in electrochemical reaction processes.

The outstanding features for the DEMS technique is its direct in situ detection for volatile products of electrochemical reaction, intermediate species as well as the properties of structure of adsorbate as a function of electrode potential or time. When more than one kinds of gases produce concomitantly on an electrode, it can detect the each faradaic current of products with the potential or time.

Key words DEMS, Mass current, On line rotating electrode inlet system, One point touch gases inlet system.

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差分电化学质谱方法(DEMS)的回顾
I. DEMS 原理和发展

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摘要　差分电化学质谱(DEMS)是将电化学和质谱技术相结合而发展起来的一种现代电化学现场测试手段. 它可现场检测电化学反应中的挥发性气体产物及动力学参数，中间体及其结构的性质等. 当电极反应产物为共析出时，DEMS技术可同时确定每种产物的法拉第电流随电极电位或时间的变化. 全文分两部分，第一部分回顾DEMS方法的原理与发展；第二部分介绍DEMS方法的应用. 本文为其中之第一部分.

关键词　DEMS方法，质量电流，旋转电极引入系统，点接触引入系统