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Electron Transfer Kinetics at Interfaces Using SECM (Scanning Electrochemical Microscopy)

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1. Introduction

Today, there is barely an aspect of our lives that is not touched fundamentally by Chemistry. We know that Chemistry is in us, because our body is composed of atoms and molecules, and functions through the extremely intricate patterns of their interactions. However, Chemistry is also around us, in natural phenomena such as photosynthesis, and in the artificial products and materials that sustain the development of our civilization: medicines, fertilizers, plastics, semiconductors, etc. Moreover, the most important global problems-those relating to food, human health, energy and the environment-cannot be solved without the aid of Chemistry.

Chemistry occupies a central position among scientific disciplines, and provides the main links between Biology and Physics. In addition, Materials Science, Chemical Engineering, Earth Sciences, Ecology, and related areas are largely based on Chemistry. And, in the near future our medical problems-and perhaps also our feelings, thoughts, and emotions-will be described and discussed on a molecular (i.e., a chemical) basis. Chemistry, in fact, is far more than a discrete scientific discipline, since its methods, concepts, and practitioners are penetrating virtually all fields of science and technology. Chemistry can, therefore, also be regarded as a trans-disciplinary science that provides an essential means and a fundamental language to understand fully these other scientific disciplines. A key feature of chemistry is chemical reactivity, and of all the chemical reactions electron transfer is undoubtedly the most important. First, electron transfer is the key step in a number of biological processes that have enormous relevance to life, such as photosynthesis and respiration. Second, it is a fundamental feature of many processes of vast technological impact, such as information storage (photography) and energy conversion (batteries). Third, electron transfer is a type of reaction that is amenable to detailed experimental investigation and accurate theoretical descriptions. But perhaps most importantly, the ubiquity of electron transfer in Chemistry and related fields has helped to demolish-and is still demolishing-the arbitrarily created barriers that until now have subdivided Chemistry into its separate organic, inorganic, physical, and analytical branches. In this respect, electron transfer encourages research at the cross-roads of different disciplines where scientific and technological progress is more likely to occur. During the past decade, our knowledge of electron transfer has grown at an astonishing rate, and it was for this reason that a need was recognised for a unified view of the field.

2. Development of SECM

Scanning electrochemical microscopy (SECM) has grown to be a powerful analytical technique for probing a wide range of interfacial processes with high spatial and temporal resolution, including heterogeneous electron-transfer reactions, molecular transport across membranes, adsorption/desorption processes, corrosion processes, the activity of living biological cells and charge-transfer at liquid/liquid interfaces. In fact, SECM is a scanning probe technique that is based on faradaic current changes when a tip is moved across the surface of a sample. This technique is useful in obtaining topographic and surface reaction kinetic information. The charge transfer is of highly importance in bioenergetics and is an active field of research. Much attention has been devoted to studying the heterogeneous electron-transfer reactions, charge transfer at liquid/liquid interfaces and molecular transport processes. SECM has recently been shown to be a valuable technique because it overcomes many typical problems, including the effects of the resistive potential drop in solution (iR drop), charging current, and allows separation of ET and IT processes at the interface between two immiscible electrolyte solutions (ITIES). Hence, analytical measurements can be performed in the interfacial region. The theory and application of SECM have been reviewed from different facets recently. In this chapter, we will discuss the basic principles of the SECM technique and chiefly focus on the latest applications of SECM to studies of charge transfer at the solid/liquid interfaces and liquid/liquid interfaces. Our group has utilized the SECM to investigate the kinetics of heterogeneous electron transfer at the modified liquid/liquid interface, liquid/solid interface by porphyrin and its derivatives.

3. Principle of SECM

3.1 Mode of operation

The illustration of an SECM instrument shown in Fig. 2 includes bipotentiostat, inchworm positioner (3D piezo positioner), electrochemical cells and data acquisition system. More detailed description of this instrument was given in literatures, such in ref (A.J. Bard, 2001). Several modes of operation of the SECM can be realized including feedback (FB) mode, tip generation/substrate collection (TG/SC) mode, substrate generation/tip collection (SG/TC) mode, penetration mode, ion transfer feedback mode, equilibrium perturbation mode, potentiometric detection mode, constant current mode, constant high mode, constant distance mode, reverse imaging mode, redox competition mode and direct mode, surface interrogation mode, microreagent mode, standing approach mode. Fig. 1 shows the mode on the SECM, the Simple model for the ET of Photosystem II in the chloroplast and three modes for SECM operation.

3.1.1 Amperometric feedback mode

The feedback mode has been widely employed to study the kinetic and imaging. In the feedback mode, the ultramicroelectrode (UME) which serves as the working electrode in a three or four-electrode system is usually called the tip. The sample that is usually called the substrate may serve as a second working electrode. The electrodes are immersed in a solution containing redox mediator (e.g., a reduced species, R). When a sufficiently positive potential is applied to the tip, O is electro-generated at a diffusion-controlled rate from solution species R to the UME Fig.1, as follow reaction (1):

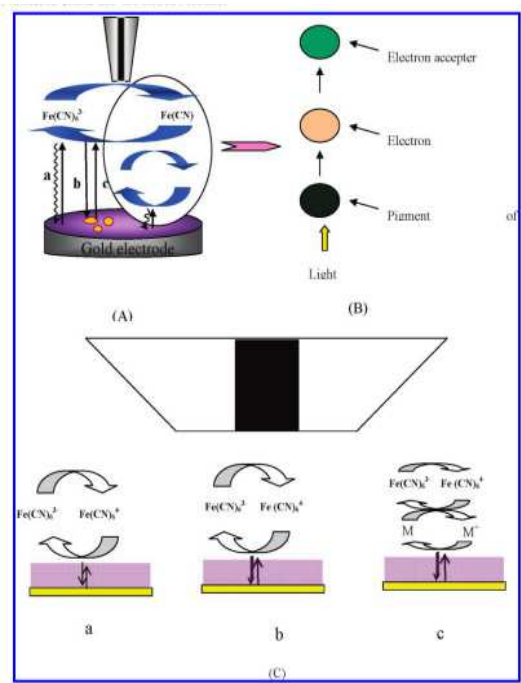
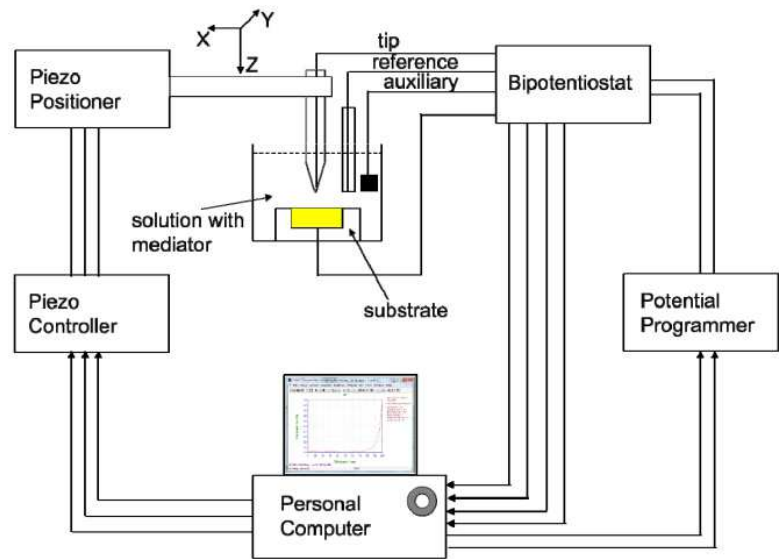


Fig. 1. (A) The Mode on SECM; (B) the Simple Model for the ET of Photosystem II in the Chloroplast; (C) Three Modes for SECM Operation: (a) Electrons of the Redox Mediator Directly Transfer through the Monolayer, Pinholes, and Defects; (b) between the Monolayer-Attached Redox Species and the Underlying Au; (c) Bimolecular Reaction between the Attached SAMs and the Redox Mediator (X.Q. Lu et al., 2010).



Scheme 1. Diagram of the scanning electrochemical microscopy (SECM) apparatus

$$R - ne^- \rightarrow O \tag{1}$$

If the tip is far (i.e., greater than several tip diameters) from the substrate, the steady-state current, $i_{T,\infty}$, for a disk-shaped tip, is given by

$$i = 4nFDca \tag{2}$$

where n is the number of electrons involved in the electrode reaction, F is the Faraday constant, D is the diffusion coefficient of R , c is the concentration of the electroactive reactant, R , and a is the radius of the ultramicroelectrode tip. When the tip is brought near a substrate, the tip current, i_T , is perturbed by hindrance of diffusion of R to the tip from the bulk solution and by reactions that occur at the substrate surface. If the tip is close to a conductive substrate, the O species formed in reaction (1) can diffuse to the substrate and be reduced back to R . When this process occurs, the flux of R to the tip is increased, and $i_T > i_{T,\infty}$. This phenomenon is termed “positive feedback” (Fig. 3a). On the other hand, when the substrate surface is an insulator or a surface where the tip generates product, O , does not react, $i_T < i_{T,\infty}$. This decrease in current is called “negative feedback” (Fig. 3b). If positive feedback measurements are carried out under diffusion-controlled condition, chronoamperometric feedback characteristics are found to be sensitive to the ratio of the diffusion coefficients of the O/R couple. But when a steady-state is established, the normalized current becomes independent of the ratio of diffusion coefficients and depends only on the tip/substrate distance. Moreover, the smaller the tip/substrate distance (d) is, the larger i_T is. The value of $i_{T,\infty}$ gives the normalizing factor for current: $i_T / i_{T,\infty}$. The approach curve is presented in from $i_T / i_{T,\infty}$ versus L (where $L = d/a$, and d is the distance between the tip and the substrate), which provides information on the kinetics of the process at the substrate. In addition, from a high-quality approach curve, one can obtain the size and shape of polished nanoelectrodes.

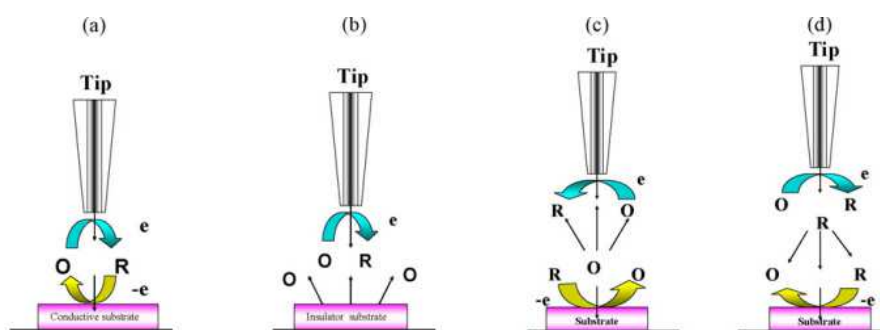


Fig. 2. Schematic diagrams of feedback mode and generation-collection mode. (a) The positive feedback mode at a conductive substrate; (b) the negative feedback mode based on hindered diffusion by insulating; (c) substrate generation/tip collection (SG/TC) mode; (d) tip generation/substrate collection (TG/GC) mode.

3.1.2 Generation/collection (TG/SC) mode

In the generation/collection (G/C) mode, both tip and substrate can be used as work electrodes, one work electrode generates some species which are collected at the other electrode. There are two significantly different G/C modes: the substrate generation/tip collection (SG/TC) mode and the tip generation/substrate collection (TG/SC) mode. The G/C mode is more sensitive because the background signal is very weak. The information about localized quantitative kinetic studies of electrode processes based on the G/C mode has been studied (R.D. Martin, 1998; A.J. Bard, 2004). The ratio of diffusion coefficients of the mediator couple may be accurately measured (R.D. Martin, 1998). Here, take the SG/TC mode as an example to explain. SG/TC is useful for measurements of concentration profiles and fluxes of either electrochemically inactive species (e.g., alkali metal ions) or species

undergoing irreversible oxidation/reduction (e.g., glucose). In SG/TC experiments, the tip transmits within a thick diffusion layer generated by the substrate. If an amperometric tip is used, the substrate diffusion is disturbed when the reaction takes place on its surface. Therefore, a potentiometric tip is usually employed in the SG/TC mode because it does not consume species and it can simultaneously diminish the disturbance to the concentration profile of electroactive species generated or consumed at the substrate. G/C imaging can be used to make high-resolution chemical concentration maps of corroding metal surfaces, biological materials, and polymeric materials.

In addition, there are still ion-transfer feedback mode, penetration mode, equilibrium perturbation mode and potentiometric detection, which are developed to investigate variously electrochemical processes.

Ion transfer feedback mode was recently developed technique by Shao and Mirkin (Y.H. Shao et al., 1997; Y. Shao., 1998). In this mode, a micropipet filled with solvent (e.g., water) immiscible with the outer solution (e.g., organic) serves as an SECM tip. The tip current is due to transfer of an ion between the pipet and the outer solution. When such a tip approaches a macroscopic liquid/liquid or liquid/membrane interface, the IT process depletes the concentration of the transferred ion near the phase boundary. If the second phase (e.g., another aqueous solution) contains the same ion, the depletion results in the IT across the interface. The tip current depends on the rate of the interfacial IT reaction, which can be extracted from approach curve. This mode is potentially useful for studies of IT reactions at and high-resolution electrochemical imaging of the liquid/liquid and liquid/membrane interfaces, and also used to study chemical properties of non-electric activity substances.

The equilibrium perturbation mode is different from other working modes, the tip is used to perturb an equilibrium at the substrate (interface) by depletion of a component of the solution. In this process, the tip current is sensitive to variation of solution equilibrium. It was used to adsorption/desorption, dissolution of ionic solids, solubility and partition equilibrium. In addition, this method can also be used to study micro-structure that cannot apply to penetrate.

The mode of potentiometric detection was applied ion selective electrode as a SECM probe to measure the varied ion concentration, and dynamic information was accessed through varied potential caused by varied ion concentration. This mode is employed to study ions that generated in enzymatic reaction and membrane permeability.

The constant current mode, constant height mode and constant distance mode of SECM imaging were useful mode for extracting important information of sample surface. In these modes, the images are obtained by scanning the tip in x, y plane above the substrate and recording the variations in z-coordinate or the tip current in solution containing either oxidized or reduced form of a redox mediator. In the constant-current mode, the current was used to control the tip-substrate separation. This constant current was unusually seted as a 70~80% of the steady-state tip current for insulator substrate or 140~150% of the steady-state tip current for conductive substrate. The tip was then scanned over the sample in the x and y directions while the tip position in the z axis was changed to maintain the tip current within 1% of the set point. A home-built digital proportional-integral-derivative (PID) loop controller using tip current as input signal and tip position as output signal was constructed

to control the vertical position of the tip during constant-current imaging. This mode was especially useful in mapping the biochemical activity of a living cell, large areas of nonflat and tilted substrates and sample consists of electroactive and nonelectroactive material. However, this mode is different from constant distance imaging of SECM, and the latter is most commonly imaging mode whereby the tip is positioned at a fixed height over the surface and scanned in the x-y plane, and the tip current versus the lateral tip positions were recorded to obtain SECM images. This work mode was potentially useful to study the enzymatic activity, modified substrate, corrosion processes, and surface catalysis and so on. In both imaging modes, it is noteworthy to identify the best initial current or set the most appropriate initial tip-substrate distance. If the set is inappropriate, this can lead to ambiguous interpretation of SECM images or tip crash and sample damage in experiment. In the constant height mode, where the tip is scanned in one plane of z-coordinate, the working distance will thus vary over rough samples. This working mode is used for studying numerous on single living cells and imaging of enzyme activity (T. Matsue et al., 2003).

Apart from these imaging modes, the reverse imaging mode (RIM) is also an important imaging method, which has been developed by White group in recent years. This is most useful for investigating transport across biological membranes (e.g., skin) and artificial membrane in situations where the SECM tip can access only the exterior membrane surface. Moreover, it is also useful in characterizing interfacial molecule or ion transfer kinetics because of the shape of RIM images is qualitatively sensitive to the rate of interfacial molecule transfer.

The redox competition mode of scanning electrochemical microscopy (RC-SECM) was first introduced by Schuhmann (K. Eckhard, 2006; W. Schuhmann, et al., 2007; W. Schuhmann, et al., 2009). It is a bipotentiostatic experiment, in which the SECM tip competes with the sample for the very same analyte. If the tip and substrate are very close to active catalyst sites, the tip current decreases. This mode was applied to investigate the electrochemical process for energy production and corrosion reactions occurring metal surface.

The direct mode of SECM is based on probing a faradaic current which flows between an ultramicroelectrode and an ionic conducting material, and has been applied successfully to microfabrication and topographical imaging of sample surface with submicrometer spatial resolution.

The surface interrogation mode of scanning electrochemical microscopy (SI-SECM) is a new in situ electrochemical technique based on scanning electrochemical microscope (SECM) operating in a transient feedback mode for the detection and direct quantification of adsorbed species on the surface of electrodes. It was used to study the adsorption phenomena in electrocatalysis and evaluate the rate constant of different redox mediators.

In the microreagent mode (W.B. Nowall et al., 1998; D.O. Wipf R et al., 2003; S. G. Denuault et al., 2005) of SECM, a reaction at the SECM tip changes the local solution composition to provide a driving force for chemical reactions at the surface. Electrolytic generation of an oxidizing agent at the SECM tip can precisely etch metal and semiconductor surfaces. Nowall et al. (W.B. Nowall et al., 1998) utilized this mode to generate micro-patterns of biotin on the electrode surface and imaged the modification with a fluorescence microscope after grafting an avidin labelled fluorophore.

The standing approach mode of SECM, in which the tip is moved vertically to first approach and then retracted from the sample surface at each measurement point, is a useful method for simultaneous electrochemical and topographic imaging of living cell and cell surface. It can avoid the damage of sample in the process of detection and image, because the tip-sample distance is controlled by feedback mechanism.

Alternating current impedance feedback and imaging of membrane pores have been investigated under alternating current scanning electrochemical microscopy (AC-SECM). AC-SECM is a versatile technique for imaging of interfacial impedance properties with high lateral resolution. Scanning electrochemical microscopy double potential step chronoamperometry (SECM-DPSC) has been developed and examined experimentally. This powerful technique supplements earlier equilibrium perturbation transient SECM methods by providing the study of the kinetics of irreversible transfer and reversible transfer processes across the ITIES.

All in all, the technology of SECM has a variety of operating modes, but it is difficult to investigate the complex systems by one of those modes in practical application. Usually, it was used by integrated application of various modes or even in conjunction with other analytical techniques to study complex problem.

3.2 Imaging surface reactivity

An important advantage of SECM is the capability to image the surface topography or reactivity by using amperometric and potentiometric probes. Two modes are used to map the surfaces of targets by SECM: the constant height mode and the constant distance mode. Constant height images are obtained by moving a probe laterally in the x and y direction above the substrate surface and monitoring the tip current, i_T , as a function of tip location. This approach is good for relatively large tip electrodes. However, when smaller tip is used in the hope of attaining higher resolution, scanning in the constant height mode becomes more difficult. The tip is possible to crash because of a change of sample height or greatly increase in surface tilt. This imaging mode is usually suitable for a flat surface or for SG/TC mode with a probe positioned far from the surface. The constant distance mode is a useful tool to provide independent information about the sample topography and monitor local electrochemical activity/conductivity in proximity of solid/liquid interfaces. In contrast, the constant distance mode can protect a tip from crashing at surface protrusions. Thus, for high resolution, SECM must be performed in the constant distance mode, as is often used with the scanning tunneling microscope (STM), where the distance is adjusted by a feedback loop to the z -piezo to maintain i_T constant. The simplest approach to constant distance imaging is the constant current mode, where the tip current is used as a feedback signal. A SECM image depending on the sample topography or reactivity can be obtained by constant current mode. Constant current imaging is straightforward when the substrate surface consists of only insulating or only conducting material. The image containing both insulating and conducting substrate is also possible using the tip position modulation (TPM) mode or the picking mode. TPM and picking modes can be used to control the tip-to-sample distance. TPM uses a small-amplitude vertical modulation of the tip position. An important aspect of this technique is that the phase of the TPM current is different for a conducting or insulating surface. In the picking mode, a surface-induced convective current is caused when the tip rapidly approaches from a large tip-substrate separation, which minimizes the

chance of tip–substrate crashes during lateral motion. In addition, the constant-impedance mode is used for distance control. Tip positioning is based on applying a high-frequency alternating voltage between the SECM tip and a counter electrode, measuring the AC current response of this system using a lock-in amplifier or frequency response analyser, and thus determining its impedance. In contrast to the constant current imaging, ac impedance imaging does not require the presence of an electroactive species in the solution. The tip impedance-based constant-distance mode has the important advantage that topography and faradaic current can be measured simultaneously. Constant distance imaging has also been showed by using a shear-force-based feedback mechanism with an optical detection system, which was developed for the positioning of an ultra small optical fiber tip in scanning near-field optical microscopy (SNOM). Using this technique, a flexible SECM tip is vibrated laterally at its resonant frequency using a piezoelectric buzzer for agitation. But the instrumentation of optical shear force-based approach is complicated. Therefore, non-optical shear-force-based detection method was developed as a highly sensitive, simple approach. It is easier to use and the operator is not limited to special electrochemical chambers and transparent solutions. Furthermore, another important approach to control tip to sample distance is the combination of atomic force microscopy (AFM) by using specially designed AFM cantilevers acting simultaneously as a force sensor for topographical AFM imaging and an UME for electrochemical SECM imaging. Because the SECM response depends on the rate of heterogeneous reaction at the substrate, it can be used to image the local surface reactivity. The resolution attainable with the SECM largely depends upon the tip radius, and the distance between tip and sample. The kinetics of several rapid heterogeneous electron-transfer reactions were measured with nanometer-sized SECM tips. Pt nanoelectrodes as SECM probes were successfully applied to improve the quality of the imaging resolution. Therefore, the resolution of the topographic imaging can be improved by reducing the size of the tip or using constant distant imaging. In addition, microelectrode arrays were used to map the surface topography or reactivity because microelectrode arrays take all the advantages of microelectrodes, including rapid response time, steady-state diffusion, and small iR drop. The applications of SECM to the imaging of surface and electrochemical system have been widely studied. It can indicate the formation process of the self-assembled monolayers (SAMs) on gold electrode at different periods and provide much electrochemical information. There is a great deal of works in this domain involving the imaging of surface reactivity and the assessment of surface reaction kinetics.

4. The kinetics of heterogeneous electron-transfer reactions

The quantitative SECM theory has been developed for various heterogeneous and homogeneous processes and different tip and substrate geometries. Especially, with the introduction of various efficient algorithms, more exact formulas have been produced by different groups. The focus of this section is on general analytical formula and numerical simulation for scanning electrochemical microscopy.

The kinetics of heterogeneous electron transfer has been the focus of considerable research activity. SECM is a powerful approach for measuring the kinetics of heterogeneous electron transfer. The kinetics of heterogeneous electron transfer can be determined with high lateral resolution while scanning a tip parallel to the surface. Distance-dependent measure ments

provide quantitative information on sample properties. Here, we only briefly presented how to extract the heterogeneous ET rate constant for approach curves. The main quantitative operation is obtained from the feedback mode. All values of tip current are normalized by the steady-state current ($i_{T,\infty}$) given in Eq. (2) for a disk-shaped tip electrode. The electron transfer rate can be obtained according to the corresponding formulas. These expressions are written in terms of a normalized current $I_T = i_T/i_{T,\infty}$, and a normalized distance, $L = d/a$. The following equations can be used to extract the rate of heterogeneous reaction occurring at a substrate:

$$I_T^k = I_S^K \left(1 - \frac{I_T^{ins}}{I_T^c}\right) + I_T^{ins} \quad (3)$$

$$I_S^K = \frac{0.78377}{L(1 + 1/\Lambda)} + \frac{[0.68 + 0.3315 \exp(-1.0672/L)]}{[1 + F(L, \Lambda)]} \quad (4)$$

Where I_T^c , I_T^k and I_T^{ins} represent the normalized currents for diffusion-controlled regeneration of redox mediator, finite substrate kinetics, and insulating substrate, respectively, and I_S^K is the kinetically controlled substrate current, $\Lambda = k_f d/D$, where k_f is the apparent heterogeneous rate constant (cm s^{-1}) and D is the diffusion coefficient, and $F(L, \Lambda) = (11/\Lambda + 7.3)/(110 - 40L)$. The analytical approximations for I_T^c and I_T^{ins} are given by following:

$$I_T^c = \frac{0.78377}{L} + 0.3315 \exp\left(\frac{-1.0672}{L}\right) + 0.68 \quad (5)$$

$$I_T^{ins} = \frac{1}{\{0.15 + 1.5385/L + 0.58 \exp(-1.14/L) + 0.0908 \exp[(L - 6.3)/1.017L]\}} \quad (6)$$

By fitting an experimental current/distance curve to theory (Eqs. (3)-(6)), the rate of an irreversible heterogeneous reaction can be obtained. The tip shape affects the approach curves because of proportional differences in lateral and normal diffusion to the tip. The steady-state and the transient currents at a hemispherical UME operating in the feedback mode of the SECM have been simulated using the alternating direction implicit finite difference method (ADIFDM). The steady-state current, $i_{T,\infty}$, at a simple hemispherical electrode is given by:

$$i_{T,\infty} = 2\pi n F D c^* a \quad (7)$$

Therefore, the approximations for the positive feedback and the negative feedback of hemispherical electrode are different from those of a disk electrode. The simulated positive and negative feedback curves can be accurately described (with an error of less than 1%), respectively :

$$I = 0.873 + \ln(1 + L^{-1}) - 0.20986 \exp\left[\frac{-(L - 0.1)}{0.55032}\right] \quad (8)$$

$$I = 0.39603 + 0.42412L + 0.09406L^2 \quad (9)$$

For $0.1 \leq F \leq 2$

In addition, SECM for localized quantitative kinetic studies of electrode reactions based on the tip generation-substrate collection operation mode was presented. The substrate current is monitored with time until it reaches an apparent steady-state value. For an irreversible first-order electrode reaction at the substrate, the analysis includes transient and steady state simulations performed using an explicit finite difference method (FDM). Transient responses, steady-state polarization curves, and TG-SC approach curves can be used to obtain substrate kinetics.

The accuracy of equation (3) is claimed by the authors as within 1-2% for $0.1 < L < 1.5$ and $0.01 < k < 1000$ for a disk microelectrode with $R_g = 10$. This theoretical formula was applied to extract the heterogeneous rate constants of complex reaction, such as charge transfer in liquid-liquid interface, electron transfer (ET) through self assembled monolayers, mediated ET in living cells, charge transport across the polymeric film enzyme mediator kinetics studies at modified substrate.

Fernandez et al. (A.J. Bard et al., 2005) has studied heterogeneous catalytic reactions using SECM feedback operating and digital simulation. They found that the tip current was strongly dependent on the stoichiometry of the substrate reaction relative to the tip reaction and extracted the rate constant of the catalytic reaction by fitting equation (10)

$$I = \frac{A_1 - A_2}{1 + \left(\frac{\kappa}{A_3}\right)^{A_4}} + A_2 \quad (10a)$$

$$A_1 = -0.00245 + 0.907 \left[1 - \exp\left(-\frac{L}{0.99}\right) \right] + 3.328 \times 10^7 \left[1 - \exp\left(-\frac{L}{3.637 \times 10^9}\right) \right] \quad (10b)$$

$$A_2 = -0.0028 + 0.972 \left[1 - \exp\left(-\frac{L}{0.48}\right) \right] + 0.4447 \left[1 - \exp\left(-\frac{L}{5.05}\right) \right] \quad (10c)$$

$$A_3 = \frac{0.261}{\frac{0.214}{L} + 1} + 0.22 \exp\left(-\frac{L + 0.034}{1.195}\right) + \left[1 - \exp\left(-\frac{L + 0.034}{0.236}\right) \right]^{3.48} \quad (10d)$$

$$A_4 = 0.7826 + 0.22 \left[1 - \exp\left(-\frac{L}{1.384}\right) \right] \quad (10e)$$

where κ is the normalized rate constant of reaction on the substrate as defined $\kappa = k_a/D$. Equation (10) was useful in treating experimental data but it doesn't have physical meaning and claimed by the authors with error less than 0.5% in the range $10^{-3} < \kappa < 10$ for an $R_g = 5$ disk UMEs.

Until now, some research groups are the rate constant from experimental data by fitting equation (3) but they ignored the R_g of the electrode used in experiment is smaller 10. Therefore, the inaccuracies and unreliability results was obtained. A new available equation (11) proposed by Lefrou (C. Lefrou et al., 2008) in 2008 used in the kinetic information extraction of SECM steady-state feedback experiment data. The accuracy of equation (3) is claimed by the authors as within $\pm 2.5\%$ for any kinetics in the condition of $L > 0.1$ for a disk microelectrode with R_g smaller than 20.

$$I_T = I_T^c \left(L + \frac{1}{\Lambda} \right) + \frac{I_T^{ins} - 1}{\left(1 + 2.47 R_g^{0.31} L \Lambda \right) \left(1 + L^{0.006 R_g} \Lambda^{-0.236 R_g + 0.91} \right)} \quad (11)$$

Where $I_T^c(L + 1/\Lambda)$ is a simple translation of I_T^c calculated by equation (12b) same L along the tip-substrate distance (L) axis and more detailed description showed in literature (C. Lefrou, 2007).

I_T^{ins} given by equation (12a) and $\Lambda = k_a L/D$ where k is the apparent heterogeneous rate constant and D is the diffusion coefficient of the redox mediator. When the R_g is equal to 10 as same as previously published literature, the new equation suitable for processing data of $L > 0.01$ and all Λ was produced and described as following: (11)

$$I_T = I_T^c \left(L + \frac{1}{\Lambda} \right) + \frac{I_T^{ins} - 1}{(1 + 5.6 L \Lambda) (1 + L^{0.177} \Lambda^{0.64})} \quad (12)$$

$$I_T^{ins} = \frac{\frac{2.08}{R_g^{0.358}} \left(L - \frac{0.145}{R_g} \right) + 1.585}{\frac{2.08}{R_g^{0.358}} (L + 0.0023 R_g) + 1.57 + \frac{\ln R_g}{L} + \frac{2}{\pi R_g} \ln \left(1 + \frac{\pi R_g}{2L} \right)} \quad (12a)$$

$$I_T^c = \alpha(R_g) + \frac{\pi}{4\beta(R_g)\arctan(L)} + \left(1 - \alpha(R_g) - \frac{1}{2\beta(R_g)} \right) \frac{2}{\pi} \arctan(L) \quad (12b)$$

In equation (12), the definition of parameters consistent with the previous equation (11). From long-term development perspective, these equations are not the ultimate perfect because of variable complex tip geometry for SECM research system. More accurate analytical equation will be generated by numerical simulation after we founded the mathematical model that was very close to research conditions. And it will be the developmental direction of SECM technology.

5. Much work about numerical simulation for SECM quantitative research

Numerical simulation is a well developed and efficient tool to treat complicated systems like microelectrodes in diffusive or convective fields. The microelectrode has been largely simulated using various numerical methods such as finite element method, finite difference method, alternating direction implicit finite-difference method, boundary element method, conformal mapping transformations and so on. The commonly general of numerical

simulation includes the following steps: (i) a numerical model of the electrochemical experimental system is set up within a computer. Specifically, this step is to build diffusion equation (Fick's second law) and find its corresponding initial and boundary conditions. (ii) According to the actual situation, an efficient and high-accuracy calculation method has been selected from the methods mentioned in previous. (iii) Write your own program and calculated or using commercially program (e.g. COMSOL Multiphysics (FEMLAB), PDEase, MATLAB) calculated. (iv) When the simulation is completed, large amounts of data are obtained. And then, one can extract from them numerical equation of current functions, concentration profiles, potential transients and so on. Comparing it with experimental results, one can obtain large numbers of useful information about complicated electrochemical problem at irregular microelectrodes and predict the results of difficult to research using general experimental methods. In addition, multidimensional integral equations (MIE) and their numerical solution can be used as an effective theoretical treatment method for microelectrode electrochemistry. Here, we mainly overview the application of numerical simulation in scanning electrochemical microscopy.

Since microelectrode is applied in electrochemical research, the simulation method has been changing from one-dimensional to multidimensional space simulation, such as in consideration of microelectrode arrays, scanning electrochemical microscopy and so on. Two-dimensional finite element method with exponentially expanding grid was first used in simulation study of SECM by Kwak and Bard (A.J. Bard et al., 1989). The theoretical current-distance curves for ring microelectrode with various R_g and a/b ratios approaching either a conductive or an insulating substrate were simulated by Lee et al. (J. Bard et al., 2001) using a commercial program PDEase2D, and they determined the size and shape of ring microelectrodes combined with experimental curves. Adaptive finite element (AFE) algorithm was introduced for use in electrochemistry and used this method to simulate the electron-flux over an arbitrarily geometry shaped SECM tips. And then they explained the simulation current deviates from linear approximation for very small distance ($L < 10^{-1}$) using 'thin-layer loss'. Using finite element analysis program PDEase2D, Zoksi et al (A.J. Bard et al., 2008) studied and analyzed theoretical SECM approach curves for UMEs with different conical geometries approaching either a conducting or insulating substrate. This research showed that the magnitude of either positive or negative feedback current decreases with increasing the aspect ratios H of finite conical electrode (i.e. $H = h/a$, the ratio of the cone height (h) to its base radius (a)). This study provided a sensitive method for extract geometric parameters including h , a and R_g of etched conical electrode for $H < 3$. A heterogeneous electron-transfer (ET) process at an unbiased conductor was studied theoretically and experimentally using SECM coupled with COMSOL Multiphysics software based on finite element method. Zhu et al. (Z. Ding et al., 2008) quantitatively analyzed variations in surface reactivity by fitting probe approach curves to curves simulated with the similar simulated method. Edwards and co-works (P.R. Unwin et al., 2009) used finite element method to investigate approach curves to a planar surface for an electrolyte-filled Scanning ion conductance microscopy (SICM) micropipet with relatively large semiangle and R_g and explored the influence factors of SICM surface topography on the current response.

A lot of research work for analytical equations for quantitative steady-state SECM experience has been carried out using conformal map transformations in recent years. Conformal mapping transformations are powerful tools for the modeling of some electrochemical

systems. This method is to transfer the original space into another better space using complex function (D. Britz, 2005), and it can be applied to extracting analytical equations from digital simulations of the microdisk SECM tip for steady-state feedback mode approach curves. The analysis provides a theoretical proof that the extraction of the kinetics parameters from experimental approach curves for quasi-reversible or irreversible kinetic reaction at the bare substrate or modified substrate. Cornut et al. (R. Cornut et al., 2010) proposed accurate analytical approximations to study microring electrode SECM approach curves in pure positive and negative feedback modes using commercially software COMSOL Multiphysics combined with MATLAB.

6. SECM measurement of the bimolecular ET reactions through molecular monolayers

A new experimental and theoretical treatment to measure the rates of ET reactions through self-assembled monolayers was developed. The bimolecular ET rate constant between a solution-base redox probe and redox centers attached to the SAMs can be determined. the general equation of ET reaction as following:



When it comes to chlorophyll electrochemistry, ET could be studied by the bimolecular reaction model and the relative rate constants. The process is described as above:

This represents the bimolecular reaction at the solid/solution interface; could be used as an electron donor, reducing matter Red₂ could be an electron acceptor, and the rate constant (k_{ox} , k_{red}) is the bimolecular oxidation-reduction rate constant ($\text{mol}^{-1} \text{cm}^3 \text{s}^{-1}$).

When the monolayer absorbed on the substrate contains an electroactive group, M, the regeneration of the mediator occurs via a bimolecular reaction with these surface-bound redox centers with a rate constant k_{BI} . The rate of the tunneling ET is governed by the relative contributions from the forward and backward reactions, k_f and k_b , which are both dependent on the value of substrate potential E_s . If bimolecular ET reaction is irreversible and the electron tunneling through the monolayer is quasi-reversible, the effective rate constant obtained from fitting an experimental approach curve to theory, k_{eff} , should be equal to:

$$k_{eff} = \frac{k_{BI} k_f \Gamma}{k_{BI} c + k_f + k_b} \quad (14)$$

Two limiting cases can occur: (a) are the formal potentials of the SAM bound redox species and redox mediator in solution, respectively. c is not very small, and E_s is not much more positive than E_{ads} . Eq. (14) becomes

$$k_{eff} \cong \frac{k_f \Gamma}{c} \quad (15)$$

In this case, the overall rate of ET is a function of k_f and c . The effective rate constant is controlled largely by the rate of tunneling through the monolayer, k_f , and is inversely proportional to c . (b) and c is small or Eq. (14) becomes

$$k_{eff} \cong k_{BI} \Gamma \quad (16)$$

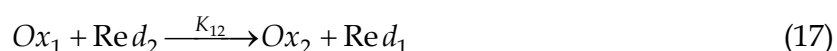
Here, the concentration and potential will not effect on k_{eff} . The overall rate of ET is limited by the bimolecular ET rate constant, k_{BI} .

7. SECM measurement of charge-transfer processes at the liquid/liquid interface

Electrochemistry at the interface between two immiscible electrolyte solutions gains more and more interest due to its wide range of applications. There is great interest in heterogeneous charge transfer (CT) reactions at the ITIES. The ITIES can serve as an SECM substrate and be probed directly by the UME. In most cases, these studies have involved four electrode systems, where the current is measured when a potential is applied across the interface. With the SECM, all electrodes are contained in a single phase, and a constant potential drop across the ITIES is controlled by the composition of the two liquid phases. Using the SECM, one can quantitatively separate interfacial ET from IT and study both processes independently. These charge transfer reactions can be classified into three main categories: (1) electron transfer, (2) simple ion transfer, (3) facilitated ion transfer.

7.1 Electron-transfer (ET) process

In a typical SECM experiment at the ITIES, studies of ET have employed the feedback mode; a tip is placed in the upper liquid phase containing one form of the redox species (e.g., the reduced form, Red_1). If the tip is held at a sufficiently positive potential, the oxidation of Red_1 at the tip occurs so as to produce the oxidised form of the species, Ox_1 . When the tip approaches to the interface, ET between the tip-generated species in phase 1 (Ox_1) and the redox-active species in phase 2 (Red_2) occurs at the interface and regenerates the original species in phase 1 (Red_1) via the bimolecular redox reaction (17)



Because i_T increases with a decrease in d , the effect of positive feedback of the regenerate species enhances the steady state current. The kinetics of such a reaction at the interface can be evaluated from the SECM approach curve. In SECM measurements, a non-polarisable ITIES is poised by the concentrations of the potential-determining ions providing a constant driving force for the ET process. To maintain electroneutrality in both phases, the transfer of common ions (either anions or cations or both) following the ET reaction occurs.

In SECM studies of ET reactions at the ITIES, there are four main steps of the over process that can influence the tip current:

1. mediator diffusion limiting current in phase 1 between the tip and the ITIES, i_T^c
2. limiting current of heterogeneous electron-transfer reaction, i_{ET} ,
3. diffusion limiting current of the redox species in phase 2, i_d ,
4. charge compensation current by IT at the interface, i_{IT} .

The electrical current across the ITIES (i_S) caused by this multistage serial process can be expressed as Eq. (18) .

$$\frac{1}{i_s} = \frac{1}{i_T^C} + \frac{1}{i_{ET}} + \frac{1}{i_d} + \frac{1}{i_{IT}} \quad (18)$$

Any of these stages can be rate-limiting, but the concentration of Red₂ is usually made sufficiently high to avoid the complication of diffusion effects in the bottom phase.

Of more interest in studies of the kinetics of ET reactions is the driving-force dependence of the rate constant. The relationship between the rate constant of ET, k_f , and the energy of activation, ΔG^\ddagger can be written as follows:

$$k_f = \text{const} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) \quad (19)$$

At low driving force, the potential dependence of the rate constant appears to follow the Butler–Volmer (B–V) theory. A Butler–Volmer type approximation can be employed:

$$\Delta G^\ddagger = -\alpha F(\Delta E^0 + \Delta \phi) \quad (20)$$

where α and F are the transfer coefficient and the Faraday constant, respectively. ΔE^0 is the difference between the standard potentials of the two-redox couples in both phases. However, at high driving force, a plot of $\log k_{12}$ versus driving force is parabolic, which is consistent with Marcus theory inverted region behavior. The Marcus theory predicts that the rate constant of an ET reaction increases when the driving force is low and decreases when the driving force is high. The inverted region of Marcus theory can be observed by a plot of $\log k_{12}$ versus the driving force. According to Marcus theory, the energy of activation for an ET reaction is given by:

$$\Delta G^\ddagger = \left(\frac{\lambda}{4}\right) \left(\frac{1 + \Delta G^0}{\lambda}\right)^2 \quad (21)$$

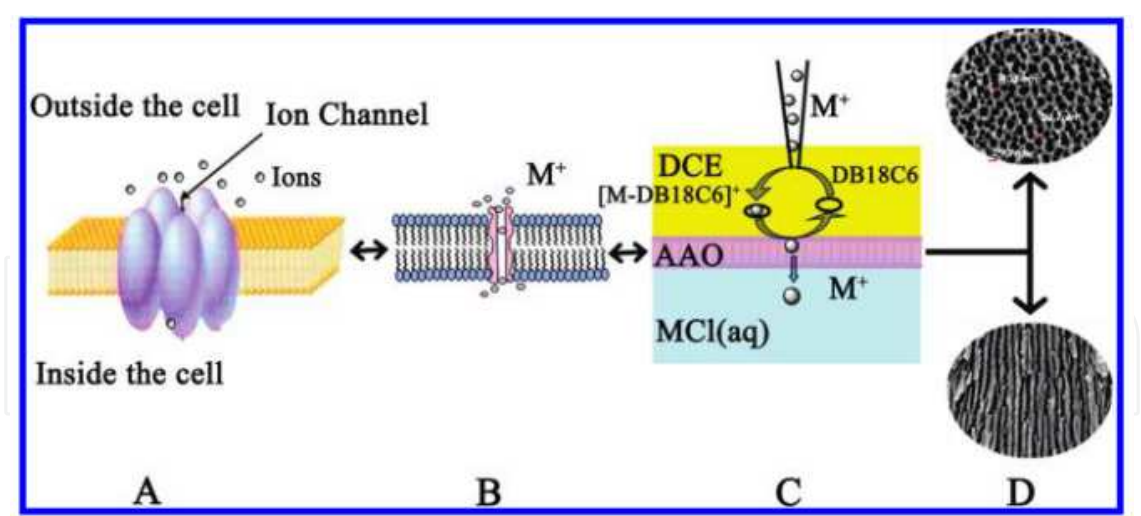
where λ is the reorganization energy, and is given by

$$\Delta G^0 = -F(\Delta E^0 + \Delta \phi) \quad (22)$$

Therefore, the activation energy of the ET reaction depend parabolically on ΔG^0 . At high driving force, the kinetics gradually comes into the Marcus inverted region and agrees with Marcus theory.

7.2 Ion transfer (IT) processes

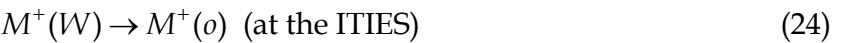
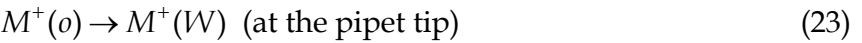
Ion transfer reactions are numerous and of importance for many biological and chemical processes, such as drug delivery, transmembrane signaling, and phase-transfer catalysis. There are two different types of IT reactions that may be studied in SECM measurements, i.e., simple (unassisted) ion transfer and facilitated ion transfer. The highly ordered porous anodic aluminumoxide (AAO) was modified at the interface between two immiscible electrolyte solutions (ITIES) to recover the process of ion transfer through the ion channels revised Scheme 3 (X.Q. Lu et al., 2010).



Scheme 2. (A) Ions through the Ion Channels; (B) Simple Model for Single Ion through the Ion Channel; (C) Model for a Three-Electrode to Investigation of Ion Transport Traversing the “Ion Channels” by (SECM); (D) Scanning Electron Micrographs of AAO

7.2.1 Simple ion transfer

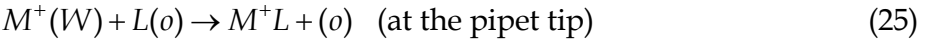
Simple IT reactions are of great importance for biological system. It can be induced in two different ways: one is to apply external potential across the interface; another is to deplete the concentration of the common ion in one of two liquid phases near the ITIES. The reaction of simple IT can be showed as follows:



In this case, both the tip and the bottom phase contain the same ion at equilibrium. M^+ is transferred from organic phase into the aqueous filling solution inside a pipet. When tip depletes concentration of this common ion in the top solvent near the ITIES, the ions transfer across the ITIES, which produces positive feedback if the bottom phase contains a sufficiently high concentration of M^+ .

7.2.2 Facilitated ion transfer

SECM is a powerful tool to probe a facilitated ion-transfer (FIT) at ITIES. The kinetics of FIT reactions has been investigated by SECM combining with micropipets or nanopipets. A micropipet filled with a solvent immiscible with the outer solution can serve as a tip electrode. The facilitated iontransfer by interfacial complexation (TIC) at the micropipet tip is:



When the concentration of M^+ inside the pipet is much higher than that of L in the organic phase and the tip is biased at a sufficiently positive potential, the reaction at the tip orifice is controlled by the diffusion of L to the interface. Subsequently, the interfacial dissociation reaction at the bottom water/oil (w/o) interface occurs. When the tip approaches the bottom

(aqueous) phase, M^+ is released from the complex and transferred into the aqueous solution and L is regenerated to its neutral form:



Although the mass-transfer rate for IT process is similar to that for heterogeneous ET process, the charge transfer processes at the tip and bottom ITIES are due to ions rather than electrons. Moreover, the tip is a pipet whose type and size strongly affect the attainable information. The smaller the pipet is, the higher mass-transfer rate that we can obtain is. The nanopipet electrodes can be fabricated and used as SECM tip (P.R. Unwin et al., 1997; A.J. Bard et al., 1999; G. Denuault et al., 1999; G. Denuault et al., 1999; G. Wittstock et al., 2002). If the ITIES formed at the pipette tip is polarizable, the driving force for the IT process is provided by the potential applied between the micropipette and the reference electrode. If the interface between the organic (top) and water (bottom) layer is non-polarizable, the Gavanian potential difference ($\Delta_O^W \phi$) at the interface is determined by the ratio of concentrations of the common ion (e.g., ClO_4^-) in the two phases.

8. Applications

8.1 Solid/liquid interface

8.1.1 ET

The study of long-distance bridge-mediated electron transfer is an important problem in electroanalytical chemistry. Self-assembled monolayers are monomolecular layers which are spontaneously formed upon immersing a solid substrate into a solution containing amphifunctional molecules. SAMs of alkanethiols have been widely used as the bridging moieties because of well-ordered, close-packed nature of the monolayer and the almost unlimited possibility of introducing functional groups in alkanethiols. Although transient electrochemical techniques, such as cyclic voltammetry, electrochemical impedance spectroscopy and chronoamperometry have been most commonly used for measuring the rates of ET through alkanethiol monolayers, these methods are affected by the resistive potential drop and double layer charging current. SECM is a useful technique for the investigation of electron transfer, eliminating problems with double layer charging and other transient contributions.

Liu et al. (A.J. Bard et al., 2004) developed a new experimental and theoretical methodology to investigate long-distance ET across molecular monolayers by SECM. The developed model can be used to independently measure the rates of ET mediated by monolayer-attached redox moieties and direct ET through the film as well as the rate of a bimolecular ET reaction between the attached and dissolved redox species by SECM. The upper limits for the electron tunneling and bimolecular rate constants measurable by the developed technique are $\sim 10^8 \text{ s}^{-1}$ and $\sim 5 \times 10^{11} \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1}$, respectively. They determined a tunneling decay constant of 1.0 per methylene group. Recently, Holt studied the electron-transfer kinetics of cytochrome c electrostatically immobilized onto a COOH-terminated alkanethiol self-assembled monolayer on a gold electrode by the technique of SECM (K.B. Holt, 2006). Approach curves were recorded with ferrocyanide as a mediator at different substrate potentials and at different coverages of cytochrome c. $k_{\text{BI}} = 2 \times 10^8 \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1}$ for the

bimolecular ET and $k^0 = 15 \text{ s}^{-1}$ for the tunneling ET are measured by the the moretical treatment proposed by Liu et al. Moreover, the kinetics of ET was also found to depend on the immobilization conditions of cytochrome c. The tunneling ET rate constant, k^0 , was found to decrease on covalent binding of the protein to them SAM and increase when mixed CH_3/COOH -terminated MLs were used.

Thiols and mercaptoalkanoic acid are often chosen in SAMs, because they can covalently link to gold surfaces by Au–S linkages to form highly ordered SAMs. The electron ransfer could be affected by the structure of the probe molecules, substrate potential and the property of the solution. Cannes et al. measured the kinetics of ferrocenemethanol electron transfer at a mono- and a bilayer-modified gold electrode. As the apparent heterogeneous rate onstant obtained at the tetradecanethiol/Au($\text{C}_{14}\text{SH}/\text{Au}$) electrode, $k^{0,\text{mono}}$ (0.02 cm s^{-1}) is larger than the value obtained at the phospholipids/tetradecanethiol/Au($\text{POPC}/\text{C}_{14}\text{SH}/\text{Au}$) electrode, $k^{0,\text{bi}}$ (0.0007 cm s^{-1}), the redox process is easier at the $\text{C}_{14}\text{SH}/\text{Au}$ electrode than at the $\text{POPC}/\text{C}_{14}\text{SH}/\text{Au}$ electrode (A.J. Bard et al., 2003). Recently, Lu et al. (X.Q. Lu et al, 2006; X.Q. Lu et al, 2006) investigated electrochemical characterization through a self-assembled monolayer of thiol-end-functionalized tetraphenyl-porphines (SH-TPP) and metal tetraphenylporphines (SH-MTPP). Different potentials on substrate controlled from 500 to 1100 mV were studied (A.J. Bard et al., 2003). The effect of substrate potential indicates that the oxidation of the porphyrins at the more positive potential is helpful to ET due to a similar bimolecular reaction between the porphyrin ring with positive charge and the probe molecules with negative charge. The reaction equation was provided as follows (X.Q. Lu et al., 2010):



The equation above can also be applied on the bimolecular reaction model for partial ET of photosystem II in the chloroplasts.

In addition, the electron transport ability of the SAMs decreased because of increased the length of the thiol-end-link spacer (alkyl group). With the insertion of metallic ions, the electron transport ability of the SAMs of SH-MTPP increased in comparison with that of the SAMs of SH-TPP (X.Q. Lu et al., 2006). The interaction between metal ions and SAMs has been studied by Burshtain and Mandler D. Mandler. 2005). They used both cyclic voltammetry and SECM techniques to investigate the binding of metal ions or protons by ω -mercaptoalkanoic acid SAMs on a gold electrode. It showed the degree of complexation affected the total charge of the monolayer and the feedback current of a charged mediator. The effect of pH on the charge transfer kinetics was also discussed. When the pH increases, the feedback current changes from positive to negative. Recently, the immobilization of ferrocenyl (Fc)-dendrimers was reported at molecular printboards via multiple host-guest interactions and the electrochemically induced desorption by SECM.

8.1.2 Immobilized enzymes

In recent years, biological samples and targets with biocatalytic activity attract a lot of interest; SECM has become a very useful technique for the study of biological systems. In particular, SECM has been devoted to studying the activity of immobilized enzymes on patterned interfaces in order to attempt to structure biosensors, chip-based assay and

enzyme immunoassays (EIAs). SECM can be used in the FB mode for imaging enzyme activity at interfaces, but the G/C mode is employed frequently because enzyme kinetics are often too slow for feedback measurements. Compare FB with G/C mode, FB shows higher lateral resolution but lower sensitivity than G/C mode. However, a new detection scheme that combines the advantages of the FB and G/C modes was proposed. This method allows high sensitivity and lateral resolution in SECM imaging. Glucose oxidase (GOx) catalyzed reaction of glucose with dissolved oxygen is often investigated in biosensor research. The oxidation of glucose catalyzed by the immobilized GOx is shown below:



The progress of this biocatalytic can be followed by detecting the hydrogen peroxide production or by detecting the decrease of oxygen concentration. Hydrogen peroxide is formed in several oxidase-catalyzed oxidations of substrates by oxygen. High currents are measured above regions of H_2O_2 production, which provides a map of GOx activity. The current increases significantly only over the immobilized GOx structures, due to the high local concentration of produced H_2O_2 during enzymatic oxidation of glucose. The glucose oxidase monolayer immobilized with an electropolymerized polyphenol film was imaged by using a μm diameter meso-porous platinum microelectrode operating in the G/C mode. The concentration distribution inside immobilized enzyme containing layers was investigated. Liquid enzyme layer immobilized with flat Cellophane membrane or cross linked polyacrylamide gel membrane containing entrapped enzyme as biocatalytic media was used in the SECM imaging. Recently, the development of chemical sensors has been focusing on the function complex multienzyme reaction layer. Csóka et al. (G. Nagy et al, 2003) studied the concentration profiles of oxygen and hydrogen peroxide recorded inside the two different enzyme layers with the SECM. The reaction layer of the amperometric enzyme sensor was made of two different parts: one was for interference elimination and the other for selective molecular recognition and measurement.

In FB imaging, a quantitative detection limit can be obtained, which indicates that the mediator concentrations and tip radius affect the limit of detection

$$k_{\text{cat}}\Gamma_{\text{enz}} \geq 10^{-3} \frac{D_{\text{Red}}C_{\text{Red}}}{a} \quad (25)$$

The left side of Eq. (25) summarizes the enzyme-dependent terms: the rate constant, k_{cat} , and the enzyme surface concentration, Γ_{enz} . In general, k_{cat} is characteristic of a particular combination of enzyme, mediator, and substrate. In the case of enzyme-loaded films, Γ_{enz} should be replaced by the product of enzyme volume concentration in the film and the film thickness. The right side of Eq. (25) presents the experimentally controllable conditions: diffusion coefficient of the mediator D_{Red} , mediator concentration c_{Red} , and the tip radius a . It indicates that low mediator concentration and large tip radius decrease the limit of detection.

Similarly to Eq. (25), there is a quantitative detection relation for the active of surface immobilized enzymes in G/C mode:

$$k_{\text{cat}}\Gamma_{\text{enz}} \geq \frac{c'D}{r_s} \quad (26)$$

where k_{cat} is the minimum catalytic reaction rate at substrate saturation, Γ_{enz} mol cm⁻² is the surface coverage of enzyme, r_s is the radius of the enzyme modified spot, c^* and D are the detection limit for the species observed at the tip and the diffusion coefficient of the detected component, respectively. This relation indicates that the sensitivity of the experiment to kinetics is increased for large sample radius r_s , low c^* , low D , and high surface coverage of enzyme.

SECM was used to study biocatalytic reactions inside the enzyme layer of a biosensor. Concentration changes of substrate, products and pH changes in the reaction layer were probed by amperometric and potentiometric tip. Many enzyme reactions and metabolic processes of microorganisms can cause pH changes. The pH sensitive antimony (Sb) tip was selected to check pH changes. The current-distance curves can be useful to give information about an optimal reaction layer thickness. These curves for both H₂O₂ and O₂ concentration profiles showed the products have local maximum inside reaction layer approximately 200 μm far from the substrate/enzyme layer boundary.

Pyrroloquinoline quinone (PQQ)-dependent glucose dehydrogenase (GDH) is of interest because of its high activity and independence of dissolved oxygen in catalyzing the transfer of electrons from glucose to an electron mediator. It can be studied by SECM using FB mode or G/C mode. Because galactosidase (Gal) which is not an oxidoreductase cannot be imaged in the conventional FB mode, it was studied in the G/C mode. Zhao and Wittstock (G. Wittstock et al, 2004) investigated a multienzyme system composed of immobilized Gal and PQQ-dependent GDH with a new detection method which combined the advantages of the FB and G/C modes and allowed high sensitivity and lateral resolution in SECM imaging. Gal and GDH were immobilized on separate batches of paramagnetic microbeads. In conventional GC imaging of Gal, p-aminophenyl-β-D-galactopyranoside (PAPG) is added to the solution, generating p-aminophenol (PAP) which can be oxidized to p-quinoneimine (PQI) under diffusion controlled conditions at the tip. The electrochemically produced PQI diffuses to the microspot, where it is reconverted into PAP by immobilized GDH in the presence of d-glucose. Therefore, SECM feedback loop was formed when PAP diffused back to the UME. The UME current, i_T , is caused by the G/C contribution from Gal and the feedback amplification by GDH. After the addition of glucose to the assay solution, a clear increase in the current strength was observed above the spot. Moreover, the peak current observed in the combined mode is about 1.8 times stronger than that observed in the conventional GC mode. Yamada et al. (Yamada, et al. 2005) have used a share force-based tip-substrate position SECM system to image a platinum-patterned array electrode and a diaphorase/albumin coimmobilized glass surface. A standing approach mode to avoid contact between the tip and the substrate was used, which repeated the approach and retraction at each data point of the surface, to obtain simultaneously both a current image and a topographic image.

8.1.3 Electrocatalytic activity

Catalyzed heterogenous reaction has been extensively investigated by SECM. Different electrode materials and pH of the solution have different catalytic activities. Hydrogen peroxide decomposition catalyzed by different solid surfaces which were catalase-modified nylon surface and Pt nanoparticles immobilized glass was performed by using an amalgam

Au-Hg disk tip. Rate constants for decomposition reaction on immobilized catalase and Pt nanoparticles were measured at different pH values. Catalase-modified nylon surface exhibited obvious activity in the pH range $5 < \text{pH} < 10$, with a maximum at around pH 7. The value of k_s is between 1×10^{-3} and $3 \times 10^{-3} \text{ cm s}^{-1}$. The activity of immobilized Pt particles (5–10 nm average diameter) showed a maximum at pH 11.9 in the pH range $10 < \text{pH} < 13$ with an apparent rate constant ($k_s = 5 \times 10^{-3} \text{ cm s}^{-1}$). Zhou et al. (A.J. Bard et al., 2000) reported the SECM feedback behavior of the H^+/H_2 mediator system at 10 mM concentrations of strong acid at different substrates and demonstrated that the feedback of the redox couple depended on the catalytic activity of the substrate surface for hydrogen oxidation. The prohibitive effect of adsorbed anions (Br^- and I^-) and reduction products of NO_3^- for catalytic H_2 oxidation on the Pt surface was also studied. The kinetics of hydrogen oxidation on Pt, Ir, and Ru substrates in acidic media was investigated. The rate constants for hydrogen oxidation on Pt ($k^\circ = 0.22 \text{ cm s}^{-1}$), Ir ($k^\circ = 0.25 \text{ cm s}^{-1}$) and Rh ($k^\circ = 0.010 \text{ cm s}^{-1}$) were obtained by fitting approach curves. The SECM can be used to quantitatively map the rate constant for the hydrogen oxidation reaction. Recently, a screening method was presented that quantitatively detects protons at a surface using the SECM. The variation in reactivity of the platinum catalyst gradient toward the hydrogen oxidation reaction was measured directly as a function of spatial position. The local rate constant value was proportional to the local platinum surface coverage. A tip reaction was employed to measure the activity of PtxRuy and PtxRuyMoz electrodeposited catalyst toward the hydrogen oxidation reaction in the absence and presence of a monolayer of carbon monoxide. The activity and the onset potential of various catalysts toward the hydrogen oxidation reaction determined by performing screening studies as a function of composition electrode potential. The use of SECM can effectively weaken the hydrogen oxidation activity and poison (CO) tolerance of the catalysts. Bard (A.J. Bard et al, 2003) detected and imaged electrocatalytic activity for the oxygen reduction reaction (ORR) in acidic medium of different electrode materials by operating in a modified TG/SC mode. When the tip placed at $30 \mu\text{m}$ from the substrate was moved in the x-y plane, activity-sensitive images of heterogeneous surfaces, e.g., with Pt and Au electrodes, were obtained from the substrate current. Moreover, the images were obtained by scanning an array of Pt and Ru spots supported on glassy carbon (Fig. 5). It showed Ru metal had weaker ORR activity than Pt. The electroactive of trodes can be sufficiently discriminated by SECM-image. Later, the heterogeneous kinetics for the ORR has been studied by TG/SC mode. The electrocatalysis of O_2 reduction at copper (II)-poly-l-histidine complex was studied and the activity of arrays of Cu^{2+} -poly-his complex spots of various compositions were imaged. After the electrocatalytic activity for the ORR of different electrode materials were studied by TG/SC mode, Fernandez et al. (A.J. Bard et al, 2005) reported the electrocatalytic activity of bimetallic (and trimetallic) materials for the ORR in acidic medium by using SECM in a new rapid-imaging mode.

8.2 Liquid / liquid interface

8.2.1 ET

The kinetics of heterogeneous electron transfer depends on the driving force at the ITIES. At low overpotential, the kinetics of ET obeys the Butler-Volmer (B-V) theory. As the driving force is increased, the Marcus inverted region appears. The existence of a Marcus inverted

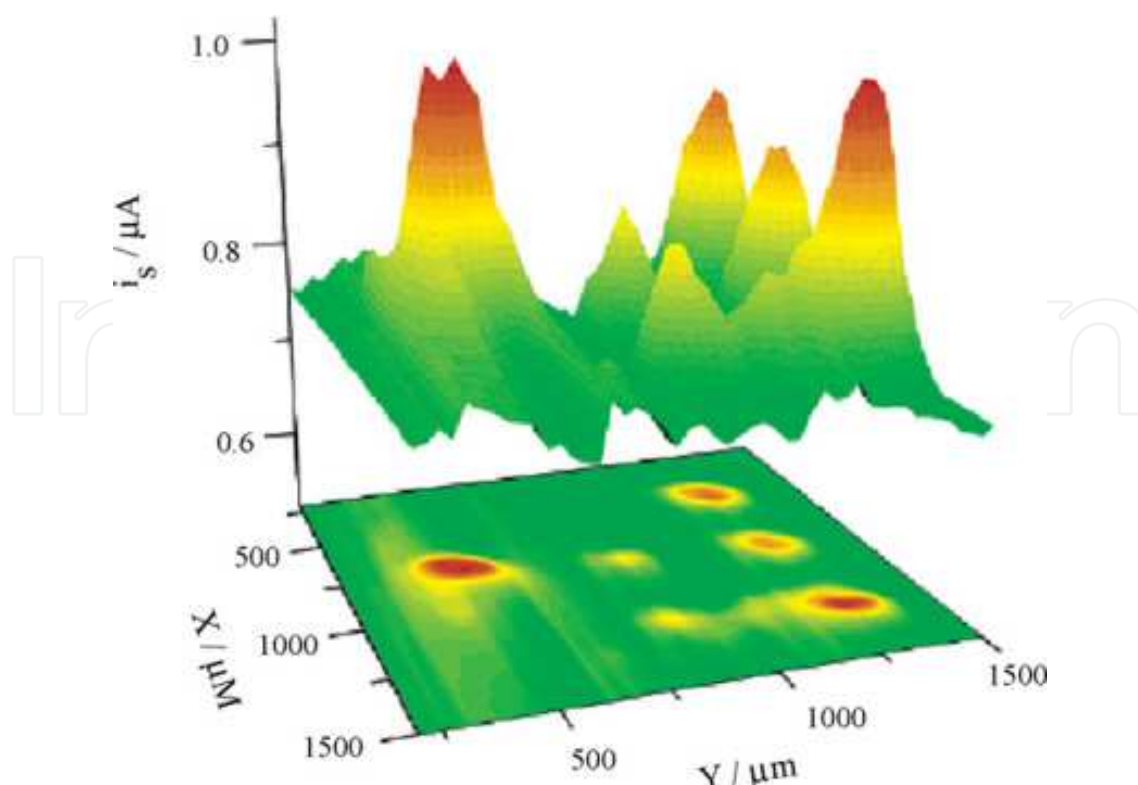
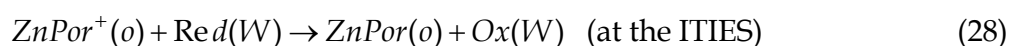
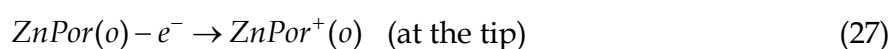


Fig. 3. ORR images obtained by the TG-SC mode of an array of Pt (left spot and right row) and Ru (middle row) spots supported on glassy carbon: scan rate $600\mu\text{ms}^{-1}$; $d = 30\text{nA}$; $i_T = 210\text{ nA}$; $ES = 0.1\text{ V}$. (A.J. Bard et al, 2003)

region at a lipid modified ITIES or unmodified ITIES was demonstrated by SECM. The previous SECM experiments were often performed with a high concentration of reactant in phase 2 compared with that of the mediator in phase 1. Barker et al. (A.L. Barker et al, 1999) developed a theoretical model that allowed the use of a relatively low concentration of the reactant in the second phase. When the concentration ratio K_r of aqueous to organic reductant ($K_r = C_{\text{Red}_2}^{*,W} / C_{\text{Red}_1}^{*,O}$) is decreased, the interfacial ET rate decreases. This approach is beneficial in studying the fast kinetic of the ET reaction. Recently, Li et al. (P.R. Unwin et al, 2007) illustrated how the use of small values of K_r is optional for fast kinetics studied and the effect of Galvani potential on the ET rate constants of the reaction between TCNQ^- and $\text{Ru}(\text{bipy})_3^{3+/2+}$ at the ITIES. The ET reaction between electrogenerated ZnPor^+ (oxidized form of zinc-21H, 23H-tetraphenylporphine) and different redox species at different water/organic solvent interfaces were studied. The redox reactions at the tip and ITIES are as follows:



where the redox couple represents $\text{Ru}(\text{CN})_6^{3-/4-}$, $\text{Mo}(\text{CN})_8^{3-/4-}$, $\text{Fe}(\text{CN})_6^{3-/4-}$, $\text{W}(\text{CN})_8^{3-/4-}$, $\text{Fe}(\text{EDTA})^{-2/-}$, $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, $\text{Co}(\text{Sep})^{3+/2+}$, and $\text{V}^{3+/2+}$.

Although the solvent used for the $\text{Fe}(\text{CN})_6^{4-}$ study was different from that of the other three reactants, the overall trend is consistent with the prediction of Marcus theory. Moreover, the

effect of aqueous ionic strength was studied by the addition of salt to the aqueous by using approach curves of SECM.

Recently, Sun et al. (Y.H. Shao et al, 2003) demonstrated the existence of an inverted region by the use of SECM with a three-electrode setup and variable concentration ratio of redox species in both phases. For the ET reaction between ZnPor in DCE and $\text{Fe}(\text{CN})_6^{3-}$ in aqueous phase, at lower applied potential ($0.54 - E_O^W < 440$ mV, E_{wo} is the externally applied potential), the increasable trend was obvious. When the applied potential (E_O^W) is given at >440 mV, the values of $\log k_{12}$ were increased slowly and reached a maximum at about 500 mV. When the driving force exceeded 600 mV, the rate constant of an ET reaction diminished (Fig. 6a). The reorganization energy ($\lambda = 47.2$ kJ mol $^{-1}$) was obtained from the best-fitting of the experimental curve. The ET reaction between TCNQ in 1, 2-dichloroethane (DCE) and $\text{Fe}(\text{CN})_6^{3-}$ in the aqueous phase was also studied (Fig. 6b). The reorganization energy is 28.9 kJ mol $^{-1}$. Compared with the studies of the forward reaction between TCNQ in DCE and $\text{Fe}(\text{CN})_6^{4-}$ in the aqueous phase, the dependence of the back ET rate constants on $\Delta_W^O \phi$ for the oxidation of TCNQ $^-$ in DCE by aqueous $\text{Fe}(\text{CN})_6^{3-}$ was studied using SECM with a fixed concentration of THAP (tetra-n-hexylammonium perchlorate) in DCE.

An interface between two immiscible electrolyte solutions is considered as the simplest model for biomembranes. There is a great deal of interest in understanding charge-transfer at modified interfaces. Amphiphilic lipid molecules dissolved in an organic phase spontaneously form a monolayer film at the water/organic interface. Although the lipids make the CT at the L/L interface more complicated, the lipid-modified interface may be a great help to study the electrical properties of membrane-bound components that control ion-transfer and electron-transfer across biological membranes. The ET reactions at lipid modified L/L interfaces have been investigated by SECM. The ET rate depends on the lipid concentration and the chain length. On the one hand, the ET rate through the ITIES decreases when the lipid concentration increases, but the ET rate reaches a limiting value and doesn't change for lipid concentrations higher than 50 Mm because of a complete lipid monolayer formed at the ITIES. On the other hand, the ET rate increases as the lipid chain length increases. The blocking effect of the lipid monolayer makes the ET rate significantly decreased. In addition, the extent of the blocking effect apparently depends on the driving force for ET process. The dependence of $\log k_f$ on driving force for ET between $\text{Fe}(\text{CN})_6^{4-}$ and ZnPor $^+$ was linear with a slope of 0.59 at lower overpotential ($\Delta E^o + \Delta_O^W \phi \leq 630$ mV). At a larger overpotential, the ET rate for Co (II) sepolchrate and V^{2+} decreased with the increasing driving force, which was consistent with Marcus theory inverted region behavior.

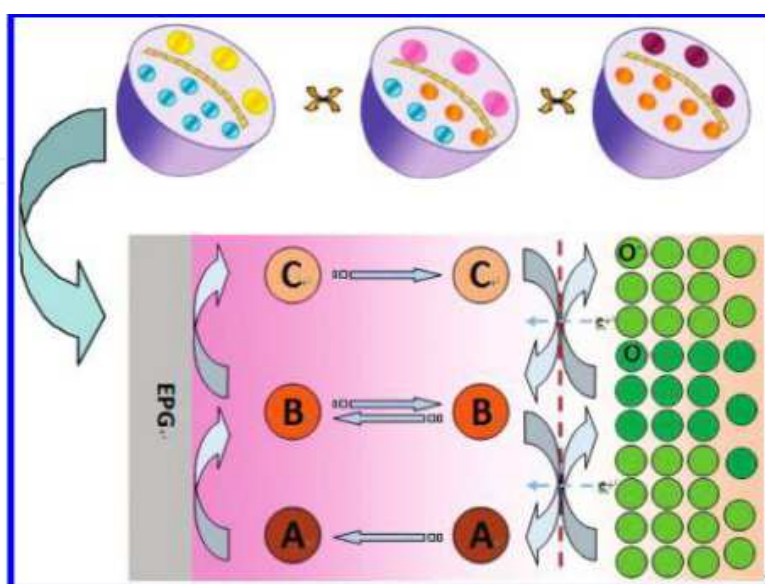
To investigate the bionic ET between dopamine (DA) and ferrocene (Fc) at the water/1, 2-dichloroethane (w/DCE) interface, the recently proposed three-electrode setup is adopted based on a glassy carbon electrode and it can be used to study the CT at a L/L interface with different phase ratios.

For an ET process, the solvent effects have recently aroused much attention, such as the effects of dielectric constants and viscosities, which mainly influence on its activation Gibbs energy and pre-exponential factor. The dependence of rate constant of the ET reaction at the interface upon the solution viscosity is evaluated using SECM. Liu and Mirkin (M.V. Mirkin et al, 1999) have investigated the effect of solvent dynamics on the rate of ET from ZnPor to $\text{Ru}(\text{CN})_6^{3-}$ using various organic solvents. The ET rate was found to be essentially independent of the potential drop across the interfacial boundary when the organic redox

reactant is a neutral species. Miao et al. (A.J. Bard et al, 2002) studied the heterogeneous electron-transfer kinetics for the oxidation of ferrocenemethanol (FcCH_2OH) over the whole composition range of dimethyl sulfoxide (DMSO)–water solutions of different viscosities (η) containing 50.0 mM $(\text{CH}_3)_4\text{NClO}_4$ (TMAP) at a Pt microelectrode by the SECM technique. Bai et al. (Y.H. Shao et al, 2003) reported the effect of solution viscosity on heterogeneous ET reaction kinetics between TCNQ and ferrocyanide. The k_{12} dependence on viscosity was explained. The ET rate constant was shown to be inversely proportional to the aqueous solution viscosity and the solvent longitudinal relaxation time, and directly proportional to the diffusion coefficient of the electroactive species. TLCV is demonstrated to be a useful means for investigating the kinetics of heterogeneous consecutive ET. (revised Scheme 3 and Fig.4) X.Q. Lu. et al. (X.Q. Lu et al., 2010) study two-step electron transfer of $\text{ZnTPP}/[\text{Fe}(\text{CN})_6]^{4-}$, indicating that the Butler-Volmer (B-V) theory is suitable for the consecutive electron transfer. This system provides an interesting example of how the relatively new theory of TLCV is used to probe more complex biological redox chemistry.

8.2.2 Ion transfer (IT) at the ITIES

Heterogeneous IT reactions are essential for many biological and technological systems. Especially, simple IT reactions are numerous and of great importance for biological systems. Wei et al. were the first to apply the SECM for investigating the IT process at the ITIES induced by ET. They demonstrated IT limitation on the overall kinetics in two cases: the organic phase without electrolyte and the effect of the concentration of the potential determining ion (TEA^+) on the shape of feedback curves. SECM is possible to probe simple (unassisted) IT reactions and map ion-transfer reactivity of the interfacial boundary with ion-transfer feedback mode of the SECM and basing some ions (mainly Na^+ and K^+), play a fundamental role in the excitability of the nerves and muscles because they are transported through the ionic channels of their cells, the ion transport traversing the “Ion Channels” was investigated by Scanning Electrochemical Microscopy (SECM). The ion-transfer feedback mode of the SECM that is used for imaging of solid/liquid and liquid/liquid interfaces has



Scheme 3. Simplified Two-Step Electron Transfer Process of Respiratory Chain in the Mitochondria and the Corresponding Reaction at the Electrode

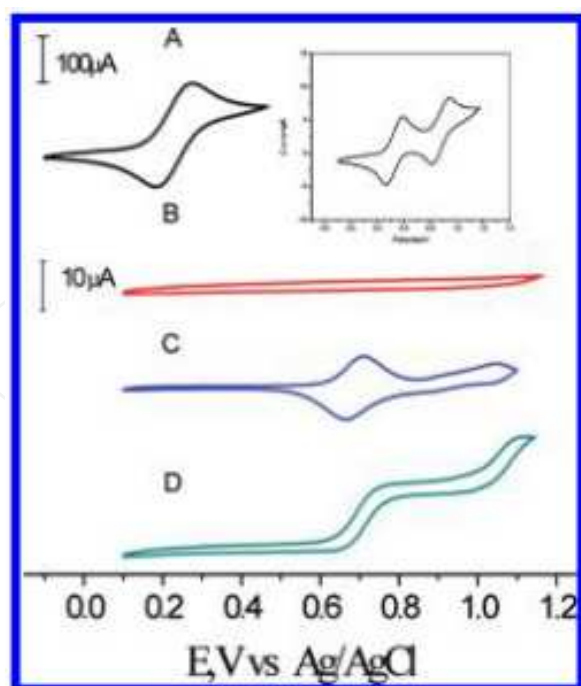
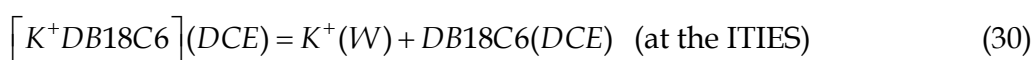
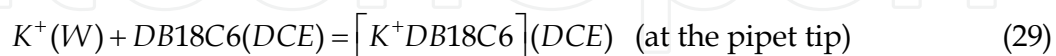


Fig. 4. Voltammetric observation of electron transfer between ZnTPP and $K_4Fe(CN)_6$. (A) Cyclic voltammogram for 10 mM $K_4Fe(CN)_6$ at an uncoated EPG electrode: (C) Cyclic voltammogram with the electrode covered with 1.5 μ L of NB containing 1 mM ZnTPP and supporting electrolyte (0.01 M $TBAClO_4$).

some advantages, including the availability of nanometer-sized pipet tips and the possibility to work without redox mediator in solution. Most IT reactions at the ITIES are often very fast and hard to measure. A mass-transfer rate sufficiently high for measurements of rapid IT kinetics under steady-state conditions can be obtained using nanometer-sized pipets based ITIES. Cai et al. measured the kinetic parameters for two rapid simple ion transfer (IT) reactions – the transfers of tetraethylammonium (TEA^+) and tetramethylammonium (TMA^+) ions between DCE and water. An excellent agreement of the k° values was obtained for the forward (from DCE to water) and reverse (from water to DCE) transfer of TEA^+ . Ion transfer across L/L interface facilitated by various types of ionophores has been extensively investigated for different cations. The process of facilitated K^+ transfer by dibenzo-18-crown-6 (DB18C6) from water into DCE has been studied extensively in the past. The reactions studied in the system can be described as follows:



The tip current was produced by the facilitated transfer of K^+ from the aqueous solution inside the pipette into DCE assisted by DB18C6. With the concentration of K^+ inside a pipette is much higher than that of DB18C6 in DCE phase, the tip current is limited by diffusion of DB18C6 to the pipet orifice. When the tip approaches the aqueous layer, DB18C6 is regenerated to its neutral form by interfacial dissociation and diffuses back to the tip to establish the feedback effect. The kinetics of these processes has been determined using

SECM combined with nanopipet and a three-electrode arrangement. A new method in which an SECM can be combined with a polarized L/L interface was introduced. Recently, the group of Shao (Y.H. Shao et al, 2006) has investigated the dependence of rate constants (k_f) on the potential drop $\Delta\phi$ of facilitated ion-transfer reaction at the W/DCE interface. The forward rate constants k_f were found to be dependent upon the driving force. When the driving force was low, the dependence of $\ln k_f$ on the driving force was linear with a transfer coefficient of about 0.3 in the case of a facilitated Na^+ -transfer reaction, which followed the classical Butler-Volmer theory. At higher driving, the Marcus inverted region was observed in the facilitated Li^+ -transfer system. In addition, it was reported that the ion transfer across the micro-water/nitrobenzene interface supported at the tip of a micropipet could be facilitated by a functionalized fullerene derivative using cyclic voltammetry (CV) and osseveryoung square wave voltammetry (OSWV).

The kinetic information about IT reactions at planar bilayer lipid membranes (BLMs) was extracted by SECM with a Pt microelectrode as the tip, where membrane permeability to conventional redox mediators was studied. The voltammetric K^+ -selective micropipet electrodes were used in the SECM feedback and generation-collection experiments to probe K^+ transfer through gramicidin channels in BLMs. Afterwards, Ti(I) can be used as a surrogate for K(I) , so that ion transport across gramicidin channels can be monitored using an amperometric UME instead of an ion-selective probe. An apparent heterogeneous rate constant ($k_{\text{het}} = 2.8 (\pm 0.1) \times 10^{-4} \text{ cm s}^{-1}$) for the transport of Ti(I) through the gramicidin to the tip was obtained. The charge transfer coupling (CTC) processes at L/L interface are common phenomena, which play an important role in many chemical and biological systems. Moreover, the processes of coupling ET-IT and IT-IT have been probed by SECM.

8.2.3 Molecular transfer

Studies of molecular transfer processes of non-charged species at the L/L interfaces can be performed by SECM. The effect of fatty alcohol monolayers on the rate constant for Br_2 transfer across the water/air (w/A) interface has been investigated using SECM-DPSC. The intracellular transfer of oxygen is of importance in bioenergetics and the diffusion of O_2 through membranes is an active area of research. The adequate supply of oxygen to cells is necessary for the growth of multicellular systems; lack of oxygen can cause cell death or necrosis. Scanning electrochemical microscopy induced transfer (SECMIT) was introduced by the Unwin's group. SECMIT is a development of the SECM equilibrium perturbation method. It can be used to characterize reversible phase transfer processes at a wide variety of interface. In other words, the SECM tip can be used to locally deplete the concentration of an electroactive species near the ITIES and induce the transfer of this species from the second liquid phase. It was shown to be a valuable method for probing the dynamics of partitioning of electroactive solutes between two immiscible phases. For the special case of slow interfacial transfer, the theory is conceptually similar to simple (unassisted) IT. Recently, SECMIT was applied to investigate the transport of molecular oxygen across phosphatidylcholine monolayers adsorbed at the interface between a buffered aqueous phase and DCE. The influence of different lipids, a series of 1, 2-diacyl-sn-glycero-3-phosphocholines (C14:0, C16:0, C18:0), on the dioxygen transfer process across the interface was studied, which demonstrated that a monolayer of C18:0 formed a barrier for the transport of a small molecule (O_2) from DCE to water but there is relatively small effect on dioxygen transfer across C14:0 and C16:0 monolayers at ambient temperature. The

interfacial rate constant decreased with increasing concentration of C18:0. This inhibited behaviour was explained in terms of a simple energy barrier mode. Cannan et al. (S. Cannan et al., 2004) have reported the kinetics of oxygen transfer across an L-R-phosphatidylethanolamine, distearoyl (DSPE) monolayer spread at three different interfaces by using SECM combined with a Langmuir trough. At all three interfaces, oxygen transfer was diffusion controlled when the monolayer was in the liquid expanded state, but the rate of transfer decreased with increasing surface pressure in the liquid condensed state. For the decane/water interfaces, oxygen transfer was diffusion-controlled up to surface pressures of approximately 20 mN m^{-1} for the thin layer and 40 mN m^{-1} for the thicker layer. At higher pressures, the rate of oxygen transfer decreased rapidly, especially at the thick decane interface. Moreover, the rate constant for oxygen transfer at thick oil/water was higher than that at thin oil/water or air/water for any given surface pressure. The phenomenon showed oxygen had an easier permeation at a thick oil/water interface where the hydrocarbon tail region of the phospholipid was less ordered (Fig. 6).

In recent years, the applications of the SECM have greatly increased in numerous fields due to the fabrication of miniaturized tips and new combinations with other techniques, for instance, with atomic force microscopy, optical microscopy (OM), single-molecule fluorescence spectroscopy (SMFS), electrochemical quartz crystal microbalance (EQCM), Langmuir trough technique, electrochemical scanning tunneling microscopy (ECSTM), scanning force microscopy (SFM) and surface plasmon resonance imaging (SPR-i). These combinations with SECM make the spatial resolution, accuracy, sensitivity further improved. In addition, more information about the topographic, optical, kinetic, or photoelectrochemical properties in situ at various interfaces can be obtained. Obviously, these combinations are to be a trend.

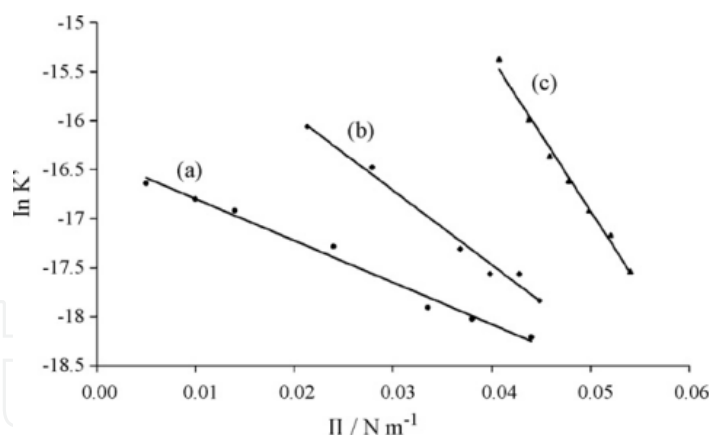


Fig. 5. Plot of $\ln k'$ vs. Π for the transfer of oxygen across a DSPE monolayer spread at the interface between (a) air/water, (b) thin decane film/water, and (c) thick decane/water (S. Cannan et al., 2004).

8.3 Photoinduced charge transfer at the solid/electrolyte interface

The use of mesoporous oxide films as a substrate to anchor the dye molecules allows sunlight to be harvested over a broad spectral range in the visible region. Similarly to chlorophyll in the green leaf, the dye acts as an electron transfer sensitizer. Upon excitation by light, it injects an electron into the conduction band of the oxide, resulting in the separation of positive and negative charges. Charge transfer from photoexcited dyes into

semiconductors was discovered more than a century ago in a famous experiment. He observed that the photoelectric effect reported earlier by Becquerel on silver plates was enhanced in the presence of erythrosin dye. A few years before, Vogel in Berlin had associated dyes with the halide semiconductor grains to make them sensitive to visible light. This led to the first panchromatic film, able to render the image of a scene realistically in black and white. However, the clear recognition of the parallelism between the two procedures, a realization that the same dyes in principle can function in both systems, and a verification that their operating mechanism is by injection of electrons from photoexcited dye molecules into the conduction band of the n-type semiconductor substrates date to the 1960s. In subsequent years the idea developed that the dye could function most efficiently if chemisorbed on the surface of the semiconductor. The concept emerged of using dispersed particles to provide a sufficient interface, then photo-electrodes were employed. Finally, the use of nanocrystalline TiO_2 films sensitized by a suitable molecular dye provided an important technological breakthrough. These mesoporous membranes have allowed in effect for the first time the development of a regenerative photoelectrochemical cell based on a simple molecular light absorber, which attains a conversion efficiency commensurate with that of silicon-based photovoltaic devices, but at a much lower cost.

The photoinduced electron-transfer (PET) processes are of vital importance in the versatility of biological and chemical systems, which exhibited extensive research prospects, such as photocatalysis, photo-to-electric conversion, photosynthesis, and photo-induced supramolecular electron-transfer (ET). Photoelectrochemical properties of porphyrin compounds, including porphyrin-fullerene dyad and ferrocene-porphyrin-fullerene triad, were investigated by self-assembled monolayers (SAMs) on nanostructured substance and electrode surfaces. With the development of SECM technology, it has been demonstrated to be an effective means of determining electron transfer (ET) kinetics on polymer films at electrodes, Langmuir monolayers at air-water interfaces, liquid-liquid interfaces, phospholipid bilayers, the traditional metal electrode-electrolyte solution interfaces, thiol-porphyrin self-assembled monolayers, as well as the semiconductor/electrolyte interface (SEI). As well all known, almost each-step ET occurring in nature can not proceed without light, indicating the studying on PET has important practical implications. Because porphyrin molecules were an important class of conjugated organic molecules for light harvesting in photosynthesis, and exhibited ultrafast electron injection, slow charge-recombination kinetics, high absorption coefficients and good chemical stability, the carboxylic groups on some porphyrins can spontaneously bind to TiO_2 nanoparticles to obtain the excellent photosensitized material (H.X. Ju et al., 2011). By fitting experimental feedback curves to theory ones, the heterogeneous rate constant (k_{eff}) is estimated, meanwhile, the dependence of k_{eff} with light source wavelength and intensity is determined (X.Q. Lu et al., 2011).

9. Scope

The scanning electrochemical microscopy has been proven to be a powerful instrument for the quantitative investigation and surface analysis of a wide range of processes that occur at interfaces. SECM has the advantage that measurements are carried out under steady-state conditions, eliminating the resistive potential drop in solution, double layer charging current and some difficulties that are frequently associated with the other traditionally electrochemical techniques. In addition, the SECM technique has provided a great advantage of easy

separation of electron transfer and ion transfer processes. These advantages of SECM make it become a versatile technique for determining electron-transfer kinetics, micropatterning and imaging of cellular activities of single cells. The development of UME and the combination of SECM and other techniques show much higher spatial resolution and precision. With the improvement of lateral resolution and sensitive detection, SECM will extend a wide variety of applications and show a great potential as analytical and microfabrication tool, especially in life sciences and in the material.

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