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## 电化学现场时间分辨FTIR 反射光谱和 程序电位阶跃暂态响应信号同步检测系统<sup>①</sup>

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**摘要** 应用弛豫(或暂态)方法研究电极过程动力学始于五十年代. 由于通过对暂态实验数据的解析能够获得反应速度常数、扩散系数、传递系数、交换电流密度等参数, 从而唯象地描述电化学反应动力学, 这一研究领域至今仍然十分活跃. 从八十年代发展起来的电化学现场红外光谱为研究电化学反应机理提供了分子水平上的数据, 从而深化了对速度控制步骤等细节的认识. 近几年来我们通过发展时间分辨电化学现场FTIR 光谱和程序电位阶跃技术成功地在分子水平上研究不可逆电化学反应的动力学, 获得中间体或产物的生成速率. 显然, 结合时间分辨红外光谱的信息和程

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序电位阶跃获得的数据将对电化学反应的机理和动力学有更深刻的认识. 迄今为止, 这两类研究都是分别进行的. 时间分辨红外光谱必须使用“薄层电解池”, 而暂态方法则应用常规的电解池, 这导致了实验条件的不一致, 从而对实验数据解析产生分歧. 理想的解决办法是两种研究方法都使用同一红外“薄层电解池”, 并且同步检测电化学反应体系的电响应(电压、电流)和光响应(红外光谱)信号. 本文报道了我们建立的同步检测系统, 并通过研究甲酸在Pt 电极上的氧化过程对该系统进行检验, 实验结果同时显示了红外“薄层电解池”的快速响应特性.

**关键词** 电化学反应动力学, 时间分辨FTIR 光谱, 程序电位阶跃技术, 同步检测系统

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## Simultaneous Detection System Combining Studies of Programmed Potential Step Technique and Time-Resolved FTIR Spectroscopy<sup>①</sup>

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The study of kinetics of electrochemical reactions using various relaxation techniques such as the potential (or current) step technique, the hydrodynamic technique etc. is an active field since the fifties<sup>[1]</sup>. This study is able to evaluate quantitatively different parameters (rate constant of reaction, diffusion coefficient, exchange current density, transfer coefficient, etc.) which describe phenomenologically the kinetics of electrochemical reaction. Nevertheless the precise determination of these parameters requires understanding the reaction mechanism or at least the rate determine step of the reaction. It may be important to point out that the investigation of mechanism of electrochemical reaction did not reach a molecular level until the last decade, in which the in situ infrared spectroscopy was invented and developed quickly<sup>[2,3]</sup>.

We have developed recently the Time-Resolved FTIR Spectroscopy (TR-FTIRS) and demonstrated<sup>[4~6]</sup> the success of studies at molecular level on the mechanism as well as the kinetics of irreversible reactions. Based on the knowledge of detailed description of reaction mechanism gained using in situ FTIR spectroscopy, the relaxation technique is used to provide new information in interpreting the kinetics of electrochemical reaction. We have illustrated that by using programmed potential step technique (PPST) the potential dependency of the rate of dissociative adsorption of small organic molecule on Pt single crystal electrodes can be determined<sup>[7~10]</sup>. The rate constant of dehydrogenation of isopropanol into acetone on these electrodes has been determined by PPST as an other example<sup>[5]</sup>.

It is evident that a well understanding on the kinetics of electrochemical reactions requires information of both TR-FTIRS and PPST. On the one hand, the results acquired from TR-FTIRS studies yield molecular description of reaction kinetics of individual intermediate or product species, and the data obtained with PPST under specific conditions can point out how fast is the rate

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determining step of reaction on the other. The investigations of TR-FTIRS and PPST were carried out, up to now, unfortunately in a separation mode, i. e. the spectra of TR-FTIRS were obtained with IR thin layer cell but the PPST data were recorded with a conventional electrochemical cell. The simultaneous recording of TR-FTIRS and PPST data with the same IR thin layer cell may be an ideal solution to avoid the divergence of experimental data obtained with different electrochemical cell (hence different conditions). In order to realise the simultaneous recording, we have built up an experimental set-up that is shown by the block diagram in Fig. 1.

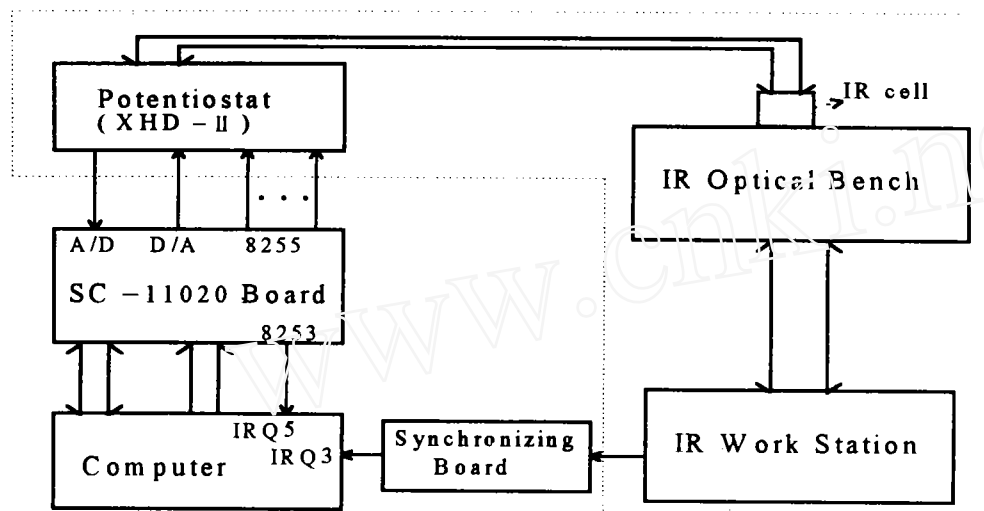


Fig. 1 Block Diagram of Simultaneous Detection System

The TR-FTIRS measurement was performed on Nicolet 730 FTIR apparatus. The experimental procedure of TR-FTIRS was fully controlled by the computer of IR work station. The electrochemical experiments were carried out with a potentiostat (XHD-II, Xiamen university) interfacing to a 386 compatible computer via a SC-11020 processing board (Beijing Square Circle Co.). The IR cell sited on the IR optical bench generates electrical response to 386 compatible computer and optical signal to IR work station. The communication and synchronisation of the two computers, that is primordial to synchronise actions of TR-FTIRS and PPST and to harmonise the measurements of the electrical and optical signals, was achieved via a home-made synchronising board. The software developed for running the simultaneous detection was written in C-language, which provides the flexibility to program the potential step signal (via DAc), to display and record data in a real time mode and to deal with acquired data ultimately.

The oxidation of formic acid on platinum electrode was studied as an example of test by using the simultaneous detection system. The different responses to a potential step from  $-0.2$  to  $0.67$  V/SCE are shown in Fig. 2. The response of electrode potential (a) to the polarisation signal yielded a very

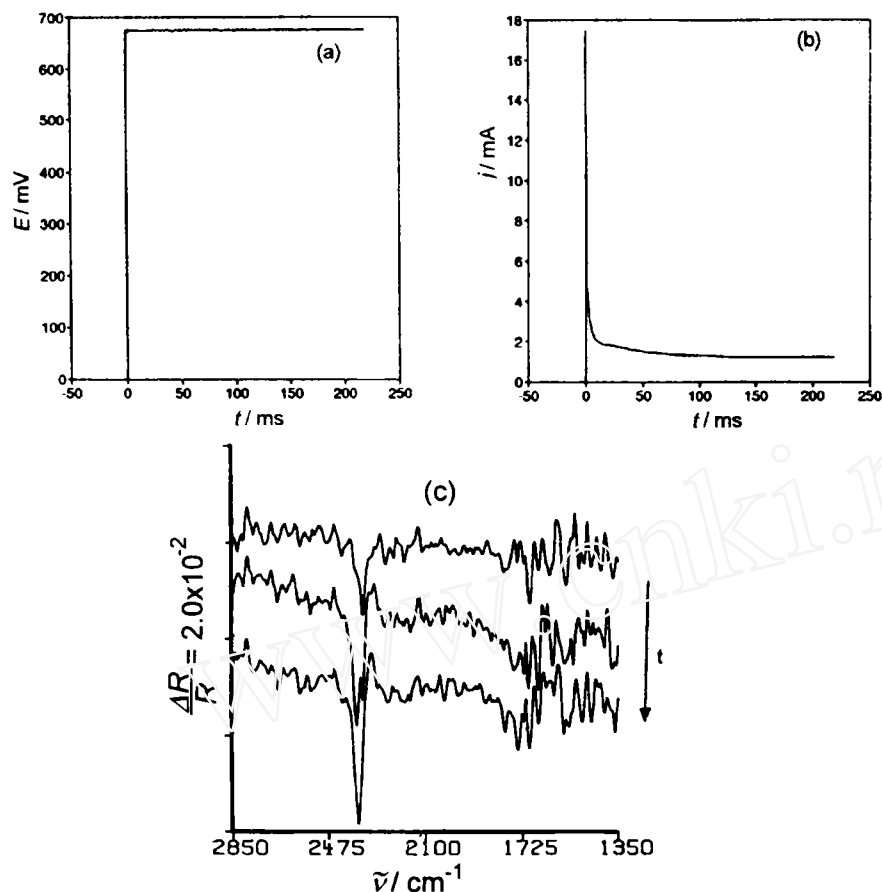


Fig. 2 Responses of the electrode potential (a), the current (b) and TR-FTIR spectra (c) for a potential step (generated by DAC) from  $-0.2$  to  $0.67$  V/SCE. Pt electrode,  $0.1$  M HCOOH +  $0.1$  M H<sub>2</sub>SO<sub>4</sub> solution

sharp edge of potential transient. The current response (b) displayed a double layer charging followed by the oxidation current. Although the platinum electrode of diameter ca.  $7.5$  mm was pushed against the IR window to form a so-called thin layer, the results of Fig. 2 a and b demonstrated that the time constant of the electrochemical IR thin layer cell is still short enough to perform kinetics studies. It is known at  $0.67$  V/SCE HCOOH can be oxidised into the final product CO<sub>2</sub>. The TR-FTIR spectra display mainly the IR band around  $2342$   $cm^{-1}$  corresponding to the asymmetrical stretching of CO<sub>2</sub> species. The increase of the intensity of CO<sub>2</sub> band with the reaction time is in good accordance with the current evolution shown in Fig. 2b. It is evident that from these experimental data we can evaluate the rate constant (Fig. 2b) and follow the kinetics features at a molecular level (Fig. 2c).

**Key words** Kinetics of electrochemical reaction, Time-resolved FTIR spectroscopy, Programmed potential step technique, Simultaneous detection system

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