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用于现场 FTIR 及 UV/Vis 光谱电化学的高质量

简单结构的光透薄层电化学池

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设计制作了一种应用于紫外可见、红外电谱电化学的新型光透薄层电化学池(OTTLE),并以铁 氰化钾水溶液、二茂铁乙腈溶液体系进行了表征。池腔儿何结构的合理设计使电位降和边缘效应降 至最低。该池有良好的伏安响应特性并可用它得到高质量的 UV/Vis 和 IR 光谱。由于简单的结构及 低廉的造价使适用于光谱电化学研究的电化学池变得更容易得到。



HIGH QUALITY OTTLE CELL WITH SIMPLE CONSTRUCTION FOR IN SITU FTIR AND UV/VIS SPECTROELECTROCHEMICAL STUDIES

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A novel optically transparent thin layer electrochemical (OTTLE) cell for ultraviolet, visible and infrared spectroelectrochemistry (SEC) was designed and characterized using ferricyanide in aqueous solutions and ferrocene in MeCN as test systems. The geometry of the cell cavity was carefully designed to minimize the ohmic potential drop and edge effect. Good voltammetric characterization and high quality spectra were obtained with the cell. The simple construction and inexpensive fabrication made it easier to obtain a cell suitable for SEC studies.

Keywords; OTTLE cell UV/Vis-SEC FT-IR SEC

0 Introduction

Spectroelectrochemical techniques are valuable methods in the field of electroanalytical chemistry^[1-3]_s By combining electrochemical techniques with various spectral methods, such as UV-Vis,</sup>

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IR, ESR, Raman etc., mor precise and detailed information can be obtained to elucidate the mechanism and kinetics of the electrochemical process^[4-7]. The majority of spectroelectrochemical (SEC) studies have been performed in the ultraviolet/visible and infrared regions. The design of a cell is very important in SEC studies. Most of the cell designs can be grouped into two categories; transmittance cell and reflectance cell, the former being more common for studies of solution species and the latter more suitable for electrode surface studies^[8]. UV/Vis SEC cell is often designed as a transmittance cell, while IR SEC cell has both kinds of designs^[8-9]. However the design for a reflectance SEC cell has some disadvantages compared with that for the transmittance cell. Fist, light throughput of the former one decreases due to reflected losses. Second, alignment of the IR beam is much more difficult if a reflectance cell is used. Furthermore the transmittance cell can be used to monitor the changes of the species in bulk solution without the interference of compounds absorbed on the electrode surface^[8]. In the various transmittance cell designs, there are many factors should be considered such as the materials of cell body, window, optic path length. Here, we specially considered the geometry of the cell cavity to minimize ohmic potential drop and edge effect. Finally the construction of the cell should be simple so that the cell can be disassembled and reassembled easily.

This paper reports the design and characterization of a novel optically transparent thin layer electrochemical (OTTLE) cell. Edge effect and ohmic potential drop of the cell are greatly minimized. Good voltammetric characterization and high quality spectra were obtained with the cell. All kinds of common windows, such as NaCl, KBr, CaF₂, monocrystalline silicon, quartz etc. can be applied and varied easily according to the wavelength range required.

1 Experiment



1.1 Cell construction

WE: Pt mini grid. CE: Pt foil. RE: Ag/AgCl or Ag foil

An illustration of the SEC cell is given in Figure 1. The SEC cell includes main body, windows. silicone rubber gaskets, and a commercially available stainless steel sample holder for IR liquid sample measurement. The main body of the cell consists of Teflon-brass clinchers, three Teflon spacers, platinum mini grid working electrode, platinum foil counter electrode and silver or AgCl-coated silver foil "pseudo-reference" electrode. Three electrodes are arranged parallelly and closely to minimize ohmic potential drop. The cell cavity is divided into three chambers. Small pathways between chambers allow electrons to flow from one chamber to the other. Solution is limited in chambers. In this way, edge effect is eliminated in a large degree with small enough ohmic potential drop. Compounds generated in the counter electrode chamber will not interfere reactions on the working electrode. Optic length of the cell is defined by spacers. Because of the low infrared molar absorption coefficient, which is about $100 \sim 1000 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$, if the cell is extra thin, the high sample concentration and the long time to collect FT-IR spectra will be needed to obtain higher sensitivity. It also causes problems such as ohmic polarization and inaccurate control of potential. In this study, the optic length we designed is 0.2 mm. The cell optic length(b) is calculated by counting the number of IR interference stripes (n) in certain region (v_1 - v_2 , cm⁻¹) for empty cell. The equation is $b = u/2(v_1-v_2)$. For the cell is assembled with a few screws it can be disassembled and reassembled easily. In this design. the pressure seal manner can ensure no leakage over the normal experimental periods. The whole cell is airtight except the two openings of the grooves. The effect of the air is small enough to ignore,

A three-electrode configuration is utilized in the cell. Working electrode is a sheet of platinum mini grid (127 wire/inch 0.9×1.5 cm² dimension and 0.11 mm thickness, 42% transmittance). Platinum foil (0, 07 mm thickness) as the counter electrode and silver foil or AgCl-coated silver foil (0, 07 mm thickness) as the pseudo reference electrode are used.

1.2 Reagents and instrumentation

Acetonitrile(AR), with 4A molecular sieves eliminating the residual water in advance, was purified by distillation. Perchlorate tetrabutylammonium (TBAP) was prepared and purified according to [10]. Ferrocene(A, R,) was purified by sublimation. Ferricyanide (A, R,) and Potassium Chloride were recrystallized from double distilled water and dried at 120 C for 24 h. Deuterated water is of G. R. grade. All other chemicals are of A, R, grade. Except the Ferrocene was dissolved in MeCN and Ferricyanide was dissolved in D₂O for 1R-SEC experiments, other solutions were prepared in water which was twice distilled in quartz distiller.

UV-Vis spectra were recorded with a UV-240 spectrophotometer (Schimadz, Japan). Infrared spectra were recorded with a Nicolet Model 5DX FT-IR spectrometer (Nicolet, USA). Electrochemical measurements of thin layer cell were performed with a Model 100B electrochemical analyzer (BAS, USA). Quartz plates were used for UV/Vis region and Potassium Bromide windows or monocrystalline silicon windows which have 58% transmission were used for infrared region.

1.3 Procedure

Solutions were prepared and thoroughly degassed by bubbling nitrogen prior to being injected into the SEC cell via hypodermic needle. A BAS-100B analyzer was employed to carry out the cyclic voltammetric experiments and the chronocoulometric experiments. Spectroelectrochemical data were • 64 •

recorded by potential-dependent mode. The spectra were recorded after the potential had been maintained for 1 min to achieve equilibrium. UV/Vis spectra were recorded corresponding to an empty reference cell. The infrared spectra were presented in the "potential difference" mode: reference spectrum was recorded at base potential (Base potential means at which species were in initial state). The difference IR spectrum was obtained by subtracting spectrum at each different potential with the reference spectrum.

2 Results and discussion

2.1 Electrochemical characterization of OTTLE cell

Figure 2(A) shows the thin layer cyclic voltammograms of ferrocyanide/ferricyanide couple in 1 mol \cdot L⁻¹ KCl solution. The cyclic voltammetric curves are symmetrical redox peak. Peak current ratio($u_{p,n}/v_{p,n}$) equal to one. As shown in table 1, with the decreasing of scan rate, the half-peak width tends to the desired value(90.6 mV) which has been derived theoretically for reversible couples under



Figure 2 (A) Thin layer cyclic voltammograms of 1.0 mmol $\cdot L^{-1} K_3 Fe(CN)$, in 1 mol $\cdot L^{-1} KCl$, scan rate/(mV/s); (a)1, (b)2, (c)3, (d)4, (e)5, (f)6, (g)7, (n)8, (l)9, (j)10 RE; Ag/AgCl foil (B) Thin layer cyclic voltammogram of 0.5 mmol $\cdot L^{-1}$ ferrocene in MeCN, 0.1 mol $\cdot L^{-1}$ TBAP, scan rate; 5 mV/s RE; Ag/AgCl foil

ideal thin layer cell condition^[11]. The peak to peak separation also tends to zero. Peak shape tends to be more symmetrical. The current is near the baseline after the peak value. Since the ohmic polarization always effects the peak width, peak to peak separation as well as peak shape, and edge effect always make the current not return to the baseline after peak value^[12], the result of the cyclic voltammogram demonstrated that the effect of ohmic polarization and edge effects are successfully restrained in great degree. The cyclic experiment was also carried out in non-aqueous solvent system(0, 1 mmol \cdot L⁻¹ ferrocene in MeCN, with 0, 1 mol \cdot L⁻¹ TBAP), which has high solution resistance. However, fairly symmetrical waves and a peak to peak separation of 15 mV at a scan tate of 1 mV/s indicated that the cell can be applied to non-aqueous systems without serious ohmic polarization effect and edge effect. The results show that the cell design permits accurate control of the potential either in aqueous or in non-aqueous systems. According to the ideal thin layer theory, the peak current (i_p) is directly proportional to the scan rate (v). In the cyclic voltammetric experiment of the ferrocyanide/ferricyanide couple $(0.5 \text{ mmol} \cdot \text{L}^{-1})$ in 1 mol $\cdot \text{L}^{-1}$ KCl solution, it was found from the plot of log i_p (A) versus log v(V/s) that, (a) when v was less than 4 mV/s, log i_p , was proportional to log v with a slop of 1 and intercept of -2. 93, (b) when v was higher than 15 mV/s, log i_{pi} was proportional to log v with a slop of 0.5 and intercept of -2. 18. The results indicate that (a) is corresponding to the pure thin layer behavior and (b) is corresponding to the pure semiinfinite diffusion control^[13]. The relation of i_p and v for reversible couples, (1) for (a) and (2) for (b), were given by [11].

v/(mV/s)	I_{pa}/mA	_{rt.e} /mA	E _{p,a} ∕m V	$E_{\rm f,c}/{\rm mV}$	$(E_{\rm p,s}+E_{\rm p,c})/2/{\rm mV}$	$\exists E_{\rm p}/mV$.3 <i>€</i> 172∎ /mV	$J\delta_{1,2r}/mV$
1	15.89	16.71	257	245	25 t	12	94	94
2	29.85	30.33	260	24ü	250	20	98	98
3	42.56	43.17	263	236	250	27	102	101
4	54.19	55.43	285	234	250	31	106	106
5	65.80	66.23	266	231	249	35	112	112
100	415.4	419.6	280	216	348	64		

Table 1	Thin Layer Cyclic	Voltammogram Data for	1 mmol • L-	¹ K ₁ Fe(CN), in 1	$mol \cdot L^{-1}$	KC1 Solution
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 $(1)_{i_0} = 9.39 \times 10^{i_0} n^2 V v C_v^*$, $(2)_{i_0} = 2.69 \times 10^{i_0} n^{2/3} A D_0^{1/2} v^{1/2} C_v^*$,

where n = 1, $D_0 = 7.6 < 10^{-6} (\text{cm}^2/\text{s})$. $A(\text{cm}^2)$ is the area of the electrode, v(V/s) is scan rate, C_a^+ (mol · L⁻¹) is the concentration of the electroactive species. V(L) is the effective volume of the thin layer cell. According to the equations, we can calculate the apparent area(A_{app}) of the mini grid electrode (3, 18 cm²) and effective volume of the cell (14, 0 µL). The calculated area approximates to the real area (2, 90 cm²) of the mini grid electrode and the calculated effective volume approximates to the result getting from the experiment of chronocoulometry for 1 mmol · L⁻¹ K₃Fe(CN)₆ in 1 mol · L⁻¹ KCl solution (16, 6 µL). It indicates that our proposal is reasonable and the cell has the high quality to certificate the theory. The results also demonstrated that at low scan rate the ohmic polarization effect was the main effect that caused the peak to peak separation and at high scan rate the contribution of the diffusion effect became more important. These facts are in good agreement with previous report^[13].

2.2 Spectroelectrochemical characterization of OTTLE cell

UV/Vis spectra for 10 mmol • L^{-1} K₃Fe(CN)₆ in 1 mol • L^{-1} KCl aqueous solution are shown in Figure 3. The absorbance changes at 418 nm and 300 nm represented the conversion of ferricyanide to ferrocyanide. The absorbance at either 418 nm or 300 nm was used to get Nernst plot. The slop of 60 mV(n=1, 03) and intercept of 0. 228 V(vs AgCl/Ag) are close to the expected value. The results indicatied the utility of this cell for UV/Vis region. Figure 4 shows the potential-dependent thin layer FTIR difference spectra for 15 mmol • L^{-1} ferrocen in MeCN, 0. 1 mol • L^{-1} TBAP system. The reversible spectra change of absorbance at 857 cm⁻¹ and 823 cm⁻¹ can be observed clearly, which demonstrated the quantitative conversion of the ferrocen/ferrocenium ion couple. The fact is in good agreement with the results that have been reported in [14].

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(A) spectra of the reduction of [Fe(CN)₆]¹⁻
(B) spectra of the oxidation of [Fe(CN)₆]¹⁻
Figure 3 UV/Vis spectra of K₃Fe(CN)₆ with potential dependent mode controlled potential, Volt (vs AgC]/Ag)

Because of the strong absorbance of water, it is difficult to carry out IR-SEC studies of aqueous system with OTTLE cell. Here, we successfully applied the cell to aqueous system. Figure 5 shows the FT-IR difference spectra for 2.7×10^{-2} mol $\cdot L^{-1} K_3 Fe (CN)_6$ in 1 mol $\cdot L^{-1} KCI$ solution. The conversion of the ion pair can be observed clearly and the quality of the spectra is as good as those obtained by SNIFTIRS (Subtractively normalized interfacial FTIR spectroscopy)^[9]. That shows the cell is suitable to be applied to aqueous system in IR-SEC study.

3 Conclusion

In summary, by comprehensively considering





different ratio factor: 1:1, scan times 10

various factors, such as ohmic polarization, edge effects, sensitivity, capability of acquired spectroscopy data, response time, airtight property and so on, we carefully designed the geometric construction of the OTTLE cell and obtained satisfactory spectroelectrochemical performance for testing compounds in aqueous and non-aqueous systems with the designed OTTLE cell. The cell has the versatility for the spectral techniques, short equilibrium time, ease of assembly and disassembly. With simple construction and inexpensive fabrication, it will be easier to construct high quality cell for SEC studies than before.





Reference spectrum was tecorded at 0, 10 V (vs AgCI/Ag). Different factor I : I, scan times 25

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