

Development of a novel electrochemical cell for slab optical waveguide spectroscopy for in situ observation of methylene blue and anions on an electrode/electrolyte interface

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Abstract

A new spectroelectrochemical cell for slab optical waveguide (SOWG) spectroscopy was developed in order to observe in situ an electrode/electrolyte interface for bulk electrolysis. The new SOWG spectroelectrochemical cell has been evaluated by simultaneous electrochemical-absorption experiments of methylene blue (MB) using cyclic voltammetry (CV) and SOWG spectrometry. CV was performed in the SOWG spectroelectrochemical cell using indium tin oxide (ITO) coated glass as the working electrode, platinum wire as the counter electrode and a silver/silver chloride electrode (Ag/AgCl) as the reference electrode. Based on the CV and SOWG spectrometric data, it was found that the SOWG spectra showed the MB spectra on the electrode surface selectively and that SOWG with the cell would be useful as a tool for in situ study of an electrode/electrolyte interface. Using this cell, the effects of the supporting electrolytes, NaNO₃, KNO₃, CH₃COONa, and CH₃COOK on the absorbance of MB were examined at the potential of +0.8 V versus Ag/AgCl. The decrease in MB absorbance by nitrate ions was greater than that of acetate ions. Therefore the competitive adsorption of nitrate ions was stronger than that of acetate ions. Thus, the decrease in absorbance of MB in the presence of anions demonstrates the competitive adsorption of anions. These results show that the extent of specific adsorption of electrolytes was observed by measuring the SOWG absorbance intensity of MB. © 2004 Elsevier B.V. All rights reserved.

Keywords: Electrochemical cell; Slab optical waveguide spectroscopy; Methylene blue; Electrode/electrolyte interface

1. Introduction

The adsorption behavior of analytes and/or electrolytes onto an electrode has been investigated by electrochemists using spectroelectrochemical methods, such as optically transparent thin-layer electrode method (OTTLE) [1,2], long optical path length thin-layer cell method (LOPTLC) [3], specular reflection method [4–6], internal reflection spectroelectrochemistry [7], ellipsometry [8–10] and infrared spectroscopy (IRS) [11]. Since OTTLE, LOPTLC, and IRS only apply to thin layer electrochemical cells, and specular reflection method and ellipsometry are not always sensitive

and selective to the electrolytes present on the interface, it is difficult to examine the specific adsorption of supporting electrolytes on an electrode/electrolyte interface during bulk electrolysis. Therefore, it is necessary to develop a new method by which an interface can be observed selectively.

Slab optical waveguide (SOWG) spectroscopy as a technique for in situ detection of molecular interaction at the liquid/solid interface is of considerable interest [12–16]. When light transmits from a media with a high refractive index, such as soda lime glass or quartz, into a media with a low index, such as water, methanol, and other solvents, at a certain incident angle, it will be totally reflected at the interface instead of transmitting through it. This results in an evanescent wave, which exponentially decreases along the interface in the low refractive index media direction. That is, only

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molecules near the interface (usually within a layer less than 100 nm in thickness) can interact with the evanescent field. So this technique provides specific determination of molecules adsorbed to the interface. For example, it has been reported that the adsorption behaviors of cytochrome *c*, myoglobin and hemoglobin on quartz and glass surface were observed by using SOWG spectroscopy [12–15]. This method can be applied to electrode surface analysis. This stimulated us to develop a new electrochemical bulk type cell for SOWG. In this investigation, a new SOWG spectroelectrochemical cell was developed and applied to the analysis of the adsorption behavior of electrolytes on an electrode/electrolyte interface during bulk electrolysis.

2. Experimental

2.1. Chemicals

Methylene blue (tetramethyl thionine, MB), KNO_3 (>99.5%), NaNO_3 (>99.0%), CH_3COOK (>98.0%), CH_3COONa (>98.5%) and KH_2PO_4 (>99.0%) were obtained from Wako Pure Chemical Industries Ltd. (Osaka, Japan) and used without further purification. Deionized and distilled water was used throughout.

2.2. SOWG spectroelectrochemical cell and SOWG spectrometry system

The SOWG spectroelectrochemical cell developed is shown in Fig. 1. An indium tin oxide (ITO) coated glass plate (15 mm \times 65 mm \times 1.0 mm, edge angle: 60°) was used as both the working electrode and the SOWG. The SOWG was mounted on the cell and the underside was in contact with a solution in a container (Daifron, 20 mm \times 50 mm \times 3.0 mm, cell volume 3.0 ml) and served as the working electrode for voltammetry. SOWG spectrometry system (SIS-50, System Instruments, Japan) was used. A Xe lamp was used as the light source. White light was coupled into the glass plate from one end of the plate and transmitted light from the other end of the plate was detected.

2.3. Cyclic voltammetry (CV) and controlled potential electrolysis

CV and controlled potential electrolysis were performed in the SOWG spectroelectrochemical cell with conventional methods. The working electrode was the ITO coated glass plate, the counter electrode was platinum wire, and the reference electrode was a silver/silver chloride electrode (Ag/AgCl). Potential to the working electrode was applied with a potentiostat (Hokuto Denko HAB-151). The electrode potential was scanned at a scan rate of 0.01 V s^{-1} . The initial potential was +0.1 V versus Ag/AgCl.

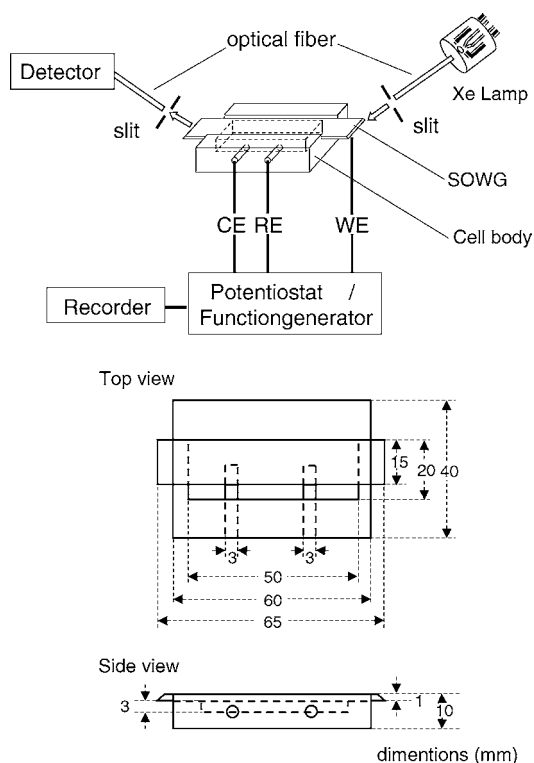


Fig. 1. Schematic diagrams of the slab optical waveguide (SOWG) spectroelectrochemical cell.

3. Results and discussion

3.1. Simultaneous measurements of cyclic voltammograms and MB SOWG spectrum

Cyclic voltammetry and SOWG spectrometry of MB were performed for evaluating the SOWG spectroelectrochemical cell developed. Fig. 2 shows the cyclic voltammogram and MB SOWG spectra of 0.5 mM MB in 100 mM KH_2PO_4 aqueous solution. When the potential was swept from -0.40 to $+0.40$ V and from $+0.40$ to -0.40 V, an anodic peak appeared at -0.21 V and a cathodic peak at -0.18 V, respectively. These peaks were due to the redox reaction of MB shown in Fig. 3. The SOWG spectra were obtained at the potential of $+0.1$ V (a), -0.1 V (b), -0.15 V (c), -0.2 V (d), -0.25 V (e) and -0.4 V (f) on the potential negative scanning and of -0.1 V (g), -0.05 V (h), -0.0 V (i), $+0.05$ V (j) and $+0.1$ V (k) on the potential positive scanning. The SOWG spectrum (a), being identical with the UV–vis spectrum of MB solution at a relatively high concentration [17], implies that oxidized MB plays a role in the interaction with the electrode surface or in the dimetric cations at the ITO electrode/electrolyte interface. The SOWG spectrum (f) had essentially no absorption between 350 and 750 nm. At that time, visual color changes of the bulk MB solution in the cell were not detected. After the following positive scan from -0.40 to $+0.40$ V, however, the same SOWG spectrum (k) as spectrum (a) reappeared. At -0.1 V, -0.15 V, -0.2 V and -0.25 V on the negative

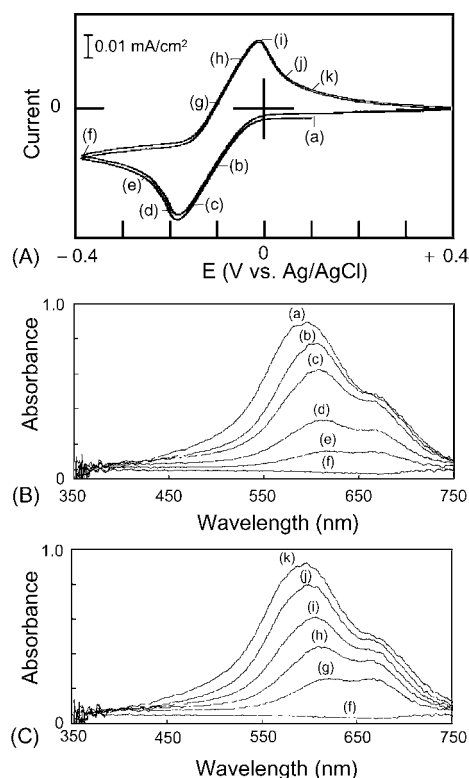


Fig. 2. Cyclic voltammogram (A) and SOWG spectra obtained on potential negative scanning (B) and on potential positive scanning (C) of 0.5 mM methylene blue (MB) in 100 mM KH_2PO_4 aqueous solution. Working electrode, indium tin oxide coated glass plate; counter electrode, platinum wire; reference electrode, silver/silver chloride electrode; initial potential, +0.1 V; scan rate, 0.01 V s^{-1} ; SOWG spectra detected at (a) +0.1 V, (b) -0.1 V, (c) -0.15 V, (d) -0.2 V, (e) -0.25 V, (f) -0.4 V, (g) -0.1 V, (h) -0.05 V, (i) -0.0 V, (j) +0.05 V and (k) +0.1 V vs. Ag/AgCl.

scanning, spectra (b), (c), (d) and (e), and at -0.1, -0.05, 0.0 and +0.05 V on positive scanning, spectra (g), (h), (i) and (j), which were medium spectra between spectrum (a) and (f), were obtained. Let us suppose that (I) the thickness of a diffusion layer, e.g., how far product molecules have moved from the electrode in a certain time, which is calculated using the following expression (1):

$$\delta = (\pi D t)^{1/2} \quad (1)$$

where D is the diffusion coefficient and t the diffusion time, is approximately $1 \mu\text{m}$, (II) the penetration depth of an evanescent wave (dp), which is calculated using the following ex-

pression (2):

$$dp = \frac{\lambda}{2\pi n_1 (\sin^2 \theta - (n_2/n_1)^2)^{1/2}} \quad (2)$$

where n_1 is the refraction index of OWG, n_2 the refraction index of the electrolyte solution, λ the wave length of incident light and θ the angle of incident light, is approximately 200 nm ($n_1 = 1.47$, $n_2 = 1.33$, $\lambda = 600 \text{ nm}$ and $\theta = 76^\circ$). Moreover the concentration profiles near the electrode during cyclic voltammetry (Fig. 4) are similar to the profile reported by Kissinger and Heineman [18]. It is understood that the intensity of absorbance near 600 nm on SOWG spectra represent the concentration near the electrode for each potential during the negative and then positive scans.

From these results, electrochemical and optical information at the electrode/electrolyte interface were available by SOWG using this cell. The repeatability of SOWG and cyclic voltammogram of 0.25 mM MB in 100 mM KH_2PO_4 were examined using the cell. As shown in Table 1, the relative standard deviation (R.S.D.) for absorbance, peak current, and peak potential less than 5% implied good of repeatability. This developed cell is easy to assemble and the installation of the electrodes to the cell is also very easy. Moreover, a SOWG spectrum has excellent repeatability as there is no strain on the waveguide from electrolyte solution pressure or the cell container. Therefore, a long waveguide can be used and bulk electrolysis can be carried out using a large cell container.

3.2. Effect of supporting electrolyte species on MB adsorption

The SOWG spectra at the positive potentials have a maximum at 600 nm . We considered that the SOWG spectra of MB were caused by all MB species present at the electrode surface and solution phase within several hundred nm from the surface. The effect of the MB species at the electrode surface on the SOWG spectra was far greater than that in the solution phase. In order to show whether oxidized MB molecules were adsorbed on the electrode surface, the following experiment was performed. The controlled potential electrolysis of the ITO electrode in 0.5 mM MB and 100 mM KH_2PO_4 was carried out at $+0.4 \text{ V}$ for 5 min . After washing the electrode with water, SOWG spectrum measurement was performed with 100 mM KH_2PO_4 aqueous solution without MB. The obtained SOWG spectrum is shown in Fig. 5. Almost the same spectrum as the spectrum (a) in Fig. 2(B) was obtained. This

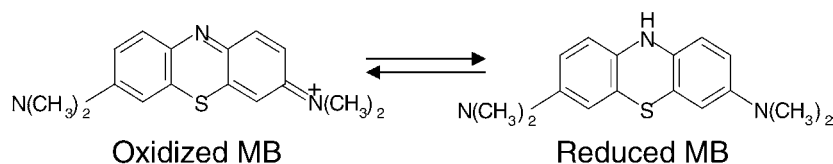


Fig. 3. Chemical structure of MB and its electrochemical reaction.

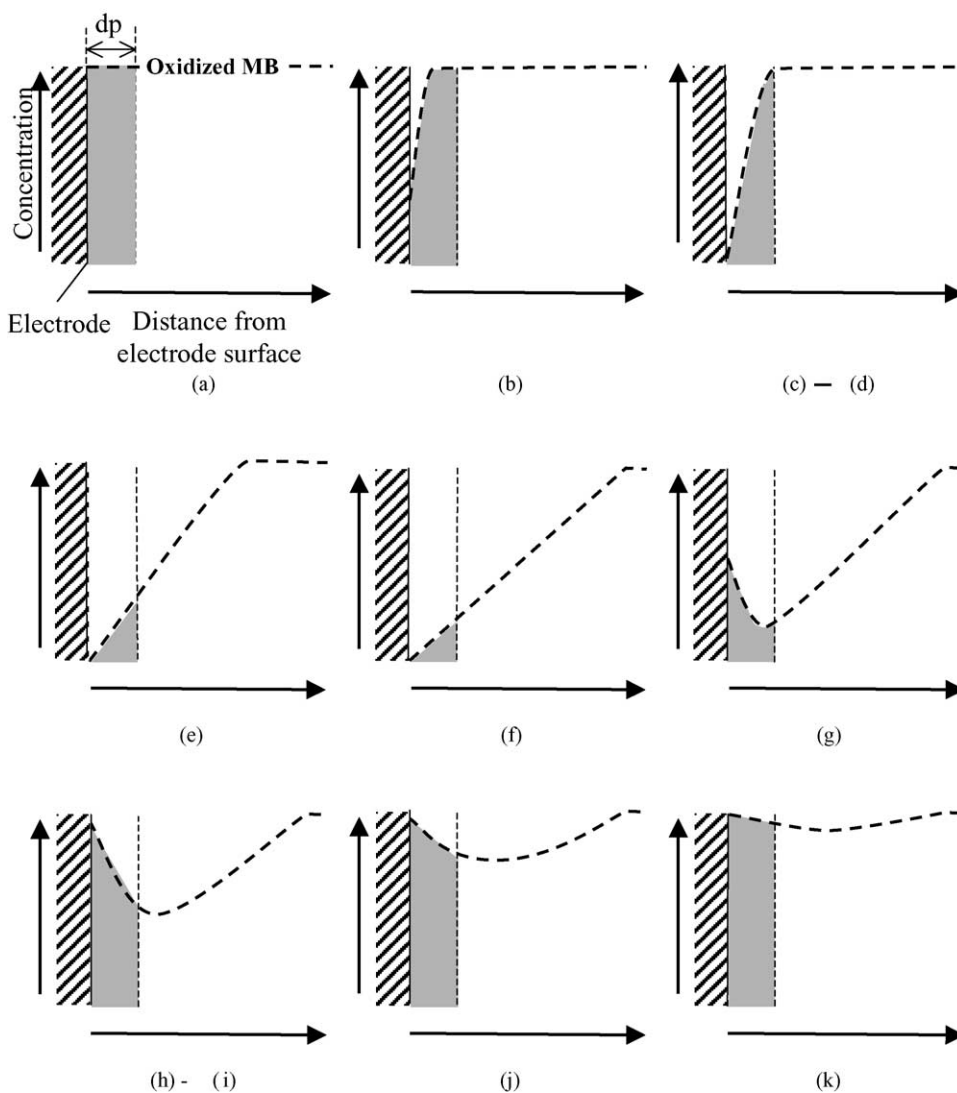


Fig. 4. Schematic illustration for concentration profiles near the electrode during cyclic voltammetry in Fig. 2(A). Shadow area shows absorbance at 600 nm of SOWG spectra in Fig. 2(B) and (C) expected to be attributed to oxidized MB molecules present near the electrode surface.

Table 1
Repeatability of absorbance on the SOWG spectra and peak currents and peak potentials on the voltammograms

	Average	R.S.D. (%) ($n = 5$)
SOWG spectra		
Absorbance ^a	0.557	4.68
Cyclic voltammograms		
Oxidation peak current	0.0213 (mA cm^{-2})	4.85
Reduction peak current	−0.0234 (mA cm^{-2})	4.01
Oxidation peak potential	−0.006 (V)	3.26
Reduction peak potential	−0.171 (V)	1.81

SOWG spectra and cyclic voltammograms were obtained at 0.25 mM MB in 100 mM KH_2PO_4 . Working electrode, indium tin oxide coated glass; counter electrode, platinum wire; reference electrode, silver/silver chloride; initial potential, +0.1 V; scan rate, 0.01 V/s; absorbance measured at 600 nm electrolysis at 0.2 V.

^a Absorbance measured at 600 nm during electrolysis at 0.2 V.

implies that the oxidized MB molecules were adsorbed on the electrode and seem to interact with the electrode surface by pi-conjugated system. Therefore, absorbance monitoring at 600 nm would give information about the characteristics of the inner helmholtz layer of an electrode/electrolyte interface. Thus, we focused on the effect of supporting electrolyte species on MB adsorption in this section. In this investigation, KNO_3 , NaNO_3 , CH_3COOK , CH_3COONa , KBr , and K_2CO_3 were used as electrolytes. However, when KBr was used as an electrolyte, MB was precipitated and when K_2CO_3 was used, MB was strongly adsorbed onto ITO electrode and could not be desorbed. So, these two species could not be examined. The effects of KNO_3 on the absorbance of MB were investigated by SOWG with the cell. When the controlled potential electrolysis of the ITO electrode in 0.5 mM MB and 10 mM

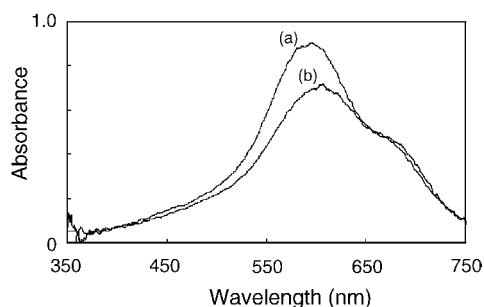


Fig. 5. When the controlled potential electrolysis of the ITO electrode in 0.5 mM MB and 100 mM KH_2PO_4 was carried out at 0.4 V for 5 min, SOWG spectrum (a) was measured. After the measurement of spectrum (a), the ITO electrode was washed with water and then the measurement of SOWG spectrum (b) was performed with 100 mM KH_2PO_4 aqueous solution without MB.

KNO_3 was carried out at +0.80 V, absorbance of 0.745 was obtained at 600 nm. With an increase in the KNO_3 concentration, the intensity of absorbance decreased, as shown in Fig. 6 (curve (a)). As electrolytes, CH_3COOK , NaNO_3 , and CH_3COONa were also examined using solutions containing 0.5 mM MB and 10 mM electrolyte. Absorbance of MB at 600 nm was 1.14 (for 10 mM CH_3COOK), 0.785 (for 10 mM NaNO_3) and 1.17 (for 10 mM CH_3COONa), respectively. The CH_3COOK , NaNO_3 , and CH_3COONa concentrations were also plotted against the absorbance as curves (b), (c) and (d) in Fig. 6. These curves imply that the electrolytes at high concentrations replaced MB and were adsorbed on the electrode surface. From these results, it is clear that the decreasing effect of the anions on the absorbance of MB was greater than that of the cations. There was strong adsorption of anions onto the inner helmholtz due to the positive potential of the electrode surface and small ion size. Furthermore, the decrease in MB absorbance by nitrate ions was greater than that of acetate ions. These results suggest that adsorbability of nitrate ions is stronger than that of acetate ions. These results correspond with the data reported by Grahame and Soderberg [19]. Therefore, MB was displaced by nitrate ions more

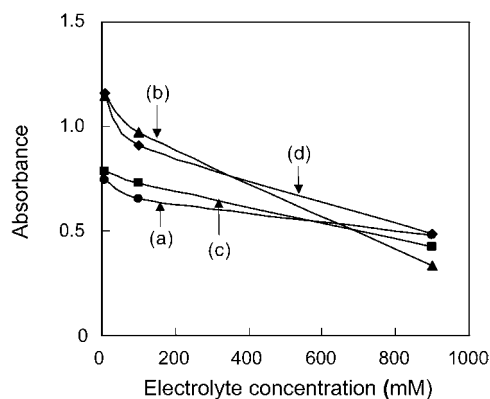


Fig. 6. Effect of KNO_3 (a), CH_3COOK (b), NaNO_3 (c), and CH_3COONa (d) concentrations on absorbance of 0.5 mM MB: controlled potential electrolysis was carried out at +0.8 V vs. Ag/AgCl.

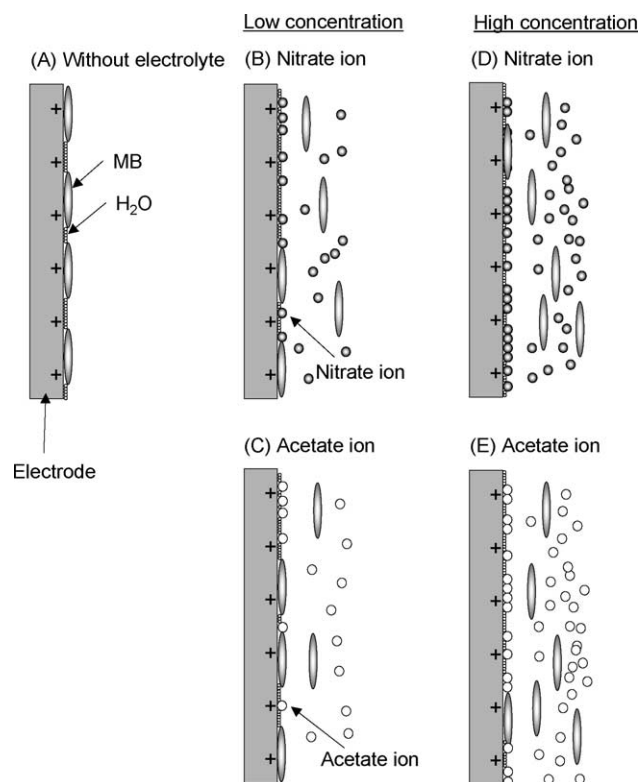


Fig. 7. Proposed model of competitive adsorption of MB and anions (A), of nitrate ions (B, D) and acetate ions (C, E).

easily than by acetate ions. Thus, the competitive adsorption of nitrate ions was stronger than that of acetate ions.

The competitive adsorption of anions and MB can be explained by the proposed models shown in Fig. 7. The electric double layer was occupied by adsorbed MB molecules with the result that SOWG absorption spectrum of MB appeared (Fig. 7(A)). When adsorbed MB molecules were replaced by acetate or nitrate ions, the absorbance at 600 nm decreased. The MB absorbance in the acetate solution was higher than in the nitrate solution (Fig. 7(B) and (C)). Thus, the replacement of nitrate ions occurred more easily than in that of the acetate ions. Almost all of the MB molecules were replaced by the anions at high concentrations (Fig. 7(D) and (E)).

As mentioned above, anions on the inner helmholtz layer which cannot be detected by UV–vis light were detected by monitoring the MB SOWG spectra.

4. Conclusion

The adsorption behavior of inorganic electrolytes on the electrode/solution interface in the bulk-type cell was observed by measuring the absorbance of MB. The data of the double layer structure was limited for the mercury electrode surface due to the lack of an appropriate method for analyzing solid electrode/electrolyte interfaces. However, the SOWG method using the new spectroelectrochemical cell for bulk electrolysis can be applied to the examination of the effects

of supporting electrolytes on the double layer existing between an ITO electrode and an electrolytic solution.

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