

奈米結構金屬氧化物修飾碳電極並應用電化學交流阻抗光譜法 於化妝品中季銨鹽含量之測定

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摘 要

製備奈米結構金屬氧化物(氧化錫、氧化鈾、氧化鈷、氧化鐵和氧化鎳)修飾碳電極作工作電極，利用電化學交流阻抗光譜法(EIS)測定季銨鹽(quaternium-73)。由交流阻抗光譜法所測得電子轉移阻抗(R_{et})隨 quaternium-73 濃度之增加而降低。電子轉移阻抗倒數 ($1/R_{et}$)對濃度作圖，求得線性關係。此線性定量測量的極限(LOQ)為 3.73 μM 。新發展的 EIS 分析法，可應用於市售化妝品中 quaternium-73 之測定。

關鍵字: 奈米結構金屬氧化物修飾碳電極，電化學交流阻抗光譜法，季銨鹽，化妝品

A novel method for quaternium-73 determination based on electrochemical impedance spectroscopy using metal oxide nano-particles modified carbon paste electrode

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ABSTRACT

A method is developed for quantitative determination of thiazolium derivative (quaternium-73) using electrochemical impedance spectroscopy (EIS). The method is based on metal oxide nano-particles (tin oxide, cerium oxide, cobalt oxide, iron oxide and nickel oxide) modified carbon paste electrodes (CPEs). An increase in the quaternium-73 concentration results in an increase in the diffusion current density of the ylidene group (= CH-R) oxidation, which corresponds to a decrease in the faradaic electron-transfer resistance (R_{et}) obtained from the EIS measurements. Quaternium-73 is quantified from linear variation of the sensor response ($1/R_{et}$) as a function of quaternium-73 concentration in solution. The method is straightforward and nondestructive. The dynamic range for determination of quaternium-73 is extended to more than two orders of magnitude. A concentration limit of quantitation (LOQ) 3.73 μM with a sensitivity of $7.58 \times 10^4 \Omega^{-1} \mu\text{M}^{-1}$ is obtained. The method is applicable to the quantitative determination of quaternium-73 in cosmetics.

Key Words: Metal oxide nano-particles modified carbon paste electrodes, electrochemical impedance spectroscopy, quaternium-73, cosmetic products

1. Introduction

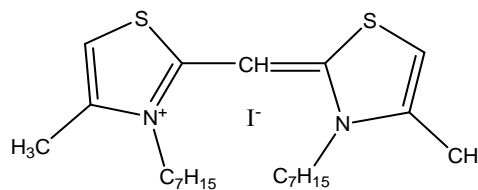
Quaternium-73 is a cyanine dye with the chemical name 3-heptyl-2-[(3-heptyl-4-methyl-3H-thiazol-2-ylidene)methyl]-4-methylthiazolium iodide. It is used as a pharmaceutical ingredient in a variety of personal care products: bactericides, and anti-acne, anti-dandruff, conditioning, and whitening agents [1-3]. Electrochemical impedance spectroscopy (EIS) is a powerful, non-destructive, and informative technique. It allows access to the complete of kinetic characteristics of electrochemical systems, such as rate constants, diffusion coefficients, and electron transfer [4-6]. Recently, EIS has been used in analytical chemistry to trace the modification steps of chemically modified electrodes based on self-assembled monolayers (SAMs) and to quantify pharmaceutical and biological species in solution. Of all the detection methods, EIS has raised the most interest because of its high sensitivity and label-free characteristics, which are uniquely attractive for biosensor and pharmaceutical analysis [7-10]. To the best of our knowledge, there are no published reports on using metal oxide nanoparticle-modified carbon paste electrodes (CPEs) based on Faradaic impedance sensors to evaluate quaternium-73. In the present work, we report on applying the EIS method using metal oxide nanoparticle-modified CPEs for quantitatively determining quaternium-73 in cosmetics.

2. Experimental

2.1 Apparatus and Materials

All electrochemical measurements were made using a potentiostat-galvanostat (SP-150; Bio-Logic SAS, Claix, France) with a conventional three-electrode configuration with a carbon fiber electrode (CFE), an unmodified CPE, and a metal oxide nanoparticle-modified CPE as working electrodes. Potentials were measured versus the Ag/AgCl electrode (RE-1; Bioanalytical Systems, West Lafayette, IN, USA), and a platinum wire was used as the auxiliary electrode.

Quaternium-73 (Scheme 1) was purchased from Hayashibara Company (Okayama, Japan). The metal oxide nanoparticles (25-100 nm) tested were tin, cerium, cobalt, iron, and nickel oxide (Sigma-Aldrich, St Louis, MO, USA). All other reagents were locally purchased and of analytical grade.



Scheme 1. Quaternium-73 structure

2.2 Electrode modification and electrochemical measurements

CPE were prepared as previously described [11]. The metal oxide nanoparticle-modified CPE electrode was produced by mixing weighed amounts of graphite powder, paraffin oil, and nano-metal oxides (0.5-3.0% w/w) thoroughly in a mortar until they were perfectly homogenized. The body of the composite metal oxide carbon paste working electrode was fabricated from a PTFE rod (optical density [o.d.]: 7 mm) with a 3-mm deep hole (diameter: 3 mm) bored into one side for the composite metal oxide carbon-paste filling. The composite metal oxide carbon paste was placed in the body of the electrode, using a PTFE spatula, and then smoothed off.

EIS were done in a phosphate buffer (pH 2.20 and 6.66), Britton and Robison buffer (pH 2.93-6.83), lithium perchlorate (LiClO_4), tetraethylammonium tetrafluoroborate (Et_4NBF_4), or tetraethylammonium perchlorate (Et_4NClO_4) solutions as supporting electrolytes at the modified CPE. EIS data acquisition were done using SP-150 (Bio-Logic SAS) and EC-Lab software. The impedance spectra were recorded over a frequency range of 0.1 Hz to 10 kHz, using a sinusoidal excitation signal, superimposed on a direct current (DC) potential of +0.180 V. Excitation amplitude of 5 mV was used throughout.

2.3 Determining quaternium-73 in cosmetics

A stock standard solution was prepared by dissolving the appropriate amount of quaternium-73 in methanol. A set of standard solutions were produced by diluting aliquots of the stock solutions with methanol to 10 mL in calibrated flasks. Taking into account the quaternium-73 content of the anti-acne cleansing gel and spray, samples (ca. 0.05 - 0.5 g) of the latter were weighed accurately in a 15-mL beaker, diluted to about 10 ml with ethyl acetate, dichloromethane, ethyl acetate-dichloromethane (3:2, v/v), and ethyl

acetate-dichloromethane (3:1, v/v), dissolved, and then centrifuged, respectively. The supernatant was transferred to a 5-mL calibrated flask. That simple dilution process worked well as the standard solution for EIS experiments.

3. Results and discussion

3.1 Choice of analytical method

The oxidation of quaternium-73 in 0.1 mol L^{-1} phosphate buffer (pH 6.66) was studied using CFE, CPE, and gold (Au) electrodes. CFE and Au electrodes exhibited an almost straight line that is characteristic of a diffusion rate-limiting step of the electrochemical process, and CPE exhibited a pronounced electrochemical Nyquist plot (Fig. 1). The charge transfer resistance was increased by the adsorption of carbon paste due to a blocking effect at the interface.

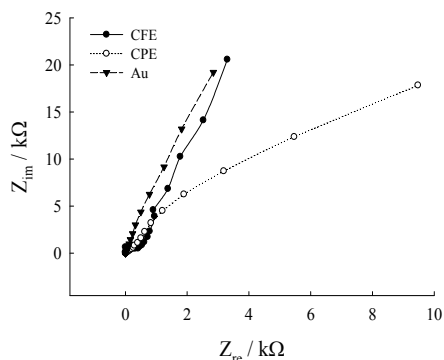


Fig. 1. Electrochemical impedance spectroscopy (EIS) of the different electrodes: carbon fiber electrode (CFE), carbon paste electrode (CPE) and gold wire electrode (Au) in phosphate buffer (pH 6.66) containing quaternium-73 ($1.48 \times 10^{-5} \text{ M}$). Scanning voltage amplitude = 5 mV, the frequency ranging from 0.1 Hz to 10 kHz.

3.2 Characteristics of metal oxide nanoparticle-modified CPEs

EIS of unmodified CPE and metal oxide nanoparticle-modified CPE were investigated at a constant concentration of quaternium-73 ($1.48 \times 10^{-5} \text{ M}$). Typical Nyquist diagrams of the CPE functionalized by different metal oxide nanoparticles immersed in the phosphate buffer (pH 6.66) are shown in Fig. 2. The impedance-plane plots of Fig. 2 are characterized by two distinct regions: (1) a semicircle in the higher frequency range related to the electron transfer process, (2) an inclined line in the complex-plane impedance plot defining a Warburg region of semi-infinite diffusion of species to the modified electrode.

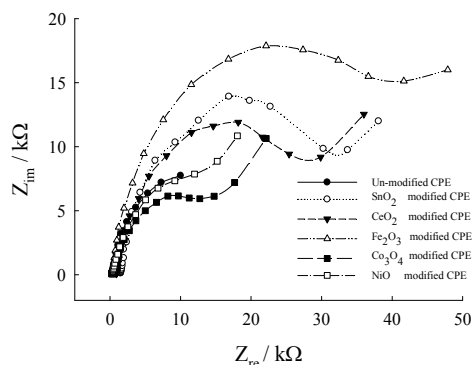


Fig. 2. Electrochemical impedance spectra: un-modified carbon paste electrode (CPE) and 1.5% metal oxide nano-particles (SnO_2 , CeO_2 , Fe_2O_3 , Co_3O_4 , and NiO) modified CPE in phosphate buffer (pH 6.66) containing quaternium-73 ($1.48 \times 10^{-5} \text{ M}$). Scanning voltage amplitude, 5 mV, the frequency ranging from 0.1 Hz to 10 kHz.

The plot exhibited a semicircle near the origin at high frequency followed by a linear tail with a slope of unity. The data can be fitted adequately by the modified Randles circuit, a well known mixed kinetic and diffusion control model [12]. The presence of metal oxide nanoparticles in the CPE improves the interaction of metal oxide with quaternium-73. Typical impedance results of the adsorbed quaternium-73 on CPEs are given in Fig. 3, where the effect of Fe_2O_3 , tin oxide (SnO_2), and cerium oxide (CeO_2) added to the CPE can be observed. These semicircles are related to the electron transfer resistance (i.e., the semicircle's diameter is equal to the electron transfer resistance [R_{et}]) and capacitance of the electrode/solution interface and are large for the adsorption of quaternium-73 (i.e., in the presence of Fe_2O_3 , SnO_2 , and CeO_2). The R_{et} of the Fe_2O_3 -modified CPE was higher than were the others. Therefore, EIS experiments were used to characterize the Fe_2O_3 -modified CPEs with different percentage ratios (0.5-2.0%). The 0.5% Fe_2O_3 displayed nearly a linear graph. When a CPE had been modified with Fe_2O_3 for different percentage ratios, the electron transfer resistance decreased significantly for the 1.0% ($R_{\text{et}} = 73 \text{ k}\Omega$), then did not slightly decrease the R_{et} with percentage ratios (1.5 - 2.0%). It is evident that a saturated nanoparticle of Fe_2O_3 was on the CPE; then, the adsorption did not change with the increase in the amount of Fe_2O_3 . A Nyquist diagram for various supporting electrolytes with the development of the Fe_2O_3 modified CPEs showed similar linear portions for each salt solution (Fig.3)— LiClO_4 , Et_4NBF_4 , and Et_4NClO_4 —which indicated that the salt of the supporting electrolytes improved the electron transfer rate between the electrode and solution. However, the

electrode in phosphate buffer (pH 6.66) generated an increase in resistance because of the change in the electrical characteristics of the electrode/electrolyte interface.

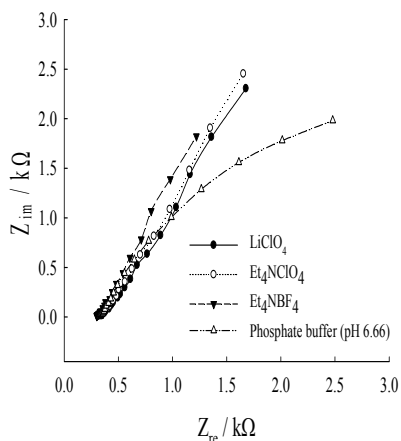


Fig. 3 Nyquist impedance spectra of a 2% Fe_2O_3 carbon paste electrodes (CPEs) in several supporting electrolytes containing quaternium-73 ($1.12 \times 10^{-4}\text{M}$). The impedance spectra were measured for lithium perchlorate (LiClO_4), tetraethylammonium tetrafluoroborate (Et_4NBF_4), tetraethylammonium perchlorate (Et_4NClO_4) and phosphate buffer (pH 6.66) solutions as supporting electrolytes.

3.3 Quantification and sensitivity

The sensitivity of the Fe_2O_3 nanoparticle-modified CPE was investigated by measuring the changes in R_{et} in various concentrations of quaternium-73. The electron transfer impedance R_{et} decreased with the concentration of quaternium-73 (Fig. 4A, B). $1/R_{\text{et}}$ has a good linear relationship with quaternium-73 concentration c in the range of $3.50 \times 10^{-6}\text{ M} - 1.12 \times 10^{-4}\text{ M}$ with the linear equation $R_{\text{et}} = 0.118 \log C - 0.031$ (unit of C , mg L^{-1}), and linear regression coefficient of 0.9943.

This observation is opposite of what we have seen for previous EIS examples, where the R_{et} has generally increased with concentrations. In order to test the applicability of the developed Fe_2O_3 nanoparticle-modified CPE, a cosmetic was analyzed using the standard addition method. The cosmetic sample was diluted with phosphate buffer, and the analytes were spiked with different concentrations of quaternium-73. A representative EIS of commercial cosmetics is shown in Fig. 5A and B.

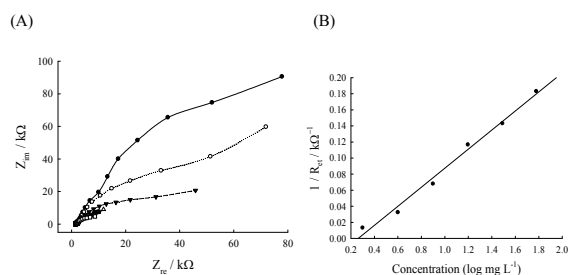


Fig. 4. (A) Nyquist plots of impedance spectra obtained on Fe_2O_3 carbon paste electrodes (CPEs) for different concentrations of quaternium-73 in phosphate buffer (pH 6.66). (B) The calibration curve obtained using $1/R_{\text{et}}$ as a function of quaternium-73 concentration at $E_{\text{DC}} = 0.18\text{ V vs. Ag/AgCl}$, linear regression equation: $Y (\text{k}\Omega) = 0.118 \log C - 0.031 (\text{mg L}^{-1})$, $R = 0.9943$.

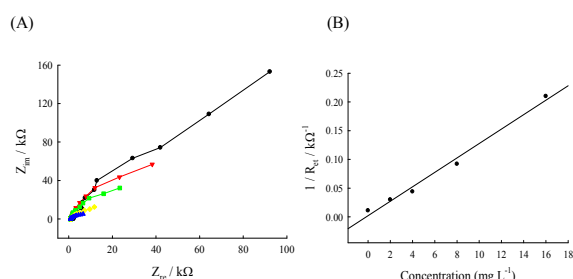


Fig. 5. (A) Nyquist plots of impedance spectra obtained from commercial cosmetics after they had been spiked with quaternium-73 solutions of 0 mg L^{-1} (black circle), 2 mg L^{-1} (red triangle), 4 mg L^{-1} (green square), 8 mg L^{-1} (yellow diamond), 16 mg L^{-1} (blue triangle). (B) The calibration plot ($R_{\text{et}} = 0.0126 x + 0.002$, $R = 0.9938$).

Conclusions

The EIS measurements of quaternium-73 were performed on various types of metal oxide (Fe_2O_3 , SnO_2 , CeO_2 , cobalt oxide [Co_3O_4], and nickel oxide [NiO]) nanoparticle-modified CPEs. We have successfully demonstrated that a Fe_2O_3 nanoparticle-modified CPE is a feasible electrode for determining quaternium-73. It exhibited a good analytical performance for the impedance detection of quaternium-73 with a low limit of quantitation, rapid response, satisfactory linear range, and good stability and selectively. The presented electrode was successfully used to determine quaternium-73 in commercial cosmetics. The method is simple and easily performed. Furthermore, the cost of using the presented electrode is lower than that of currently used methods.

Acknowledgments

This work was financially supported by grant NSC 99-2113-M-041-001-MY3 from the National Science Council, Taiwan ROC.

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