DOCTORAL THESIS

Studies on the preparation and electroanalytical applications of chemically modified electrodes

Song, Fayi

Date of Award:
2000

Studies on the Preparation and Electroanalytical Applications of Chemically Modified Electrodes

SONG Fayi

A thesis submitted in partial fulfillment of the requirements

for the degree of

Doctor of Philosophy

January 2000

Hong Kong Baptist University

ABSTRACT

Chemically Modified Electrodes (CMEs) has been the subject of intense research in electrochemistry and electroanalytical chemistry. Our interests are to develop novel types of CMEs and to study the possible applications in analytical chemistry. The present work focuses on the studies of the preparation and electroanalytical applications of the electrochemically activated glassy carbon electrode (PGCE) and electropolymerized polypyrrole (PPy) film modified glassy carbon electrodes. The electroanalytical applications involved voltammetric and potentiometric responses of the CMEs obtained.

A good reproducible activated glassy carbon electrode was obtained by electrochemical pretreatment. We have reported in chapter 2, possibly the first work on the electroanalytical applications of the PGCE. Electrochemically activated glassy carbon electrodes adsorbed with alizarin red S (ARS) were applied in the electroanalysis of metal species. Copper species were readily extracted onto the ARS modified electrodes and were determined electrochemically. Experimental results showed that the voltammetric peak current resulted from copper incorporation on ARS modified electrodes was significantly larger than that obtained on bare activated electrodes. Voltammetric peak currents showed linear response for copper concentrations in the range between 0.001 to 0.15 mM with a large slope of 1.77 A M^{-1} and a correlation coefficient of 0.998. The reproducibility of the voltammetric measurements was found to be within 10% RSD for five replicate measurements on copper concentration of 0.10 mM. The modified electrodes could be applied for repeated copper determinations without appreciable deterioration in electrode response.

Many species of polycyclic aromatic hydrocarbons substituted with one or more nitro-groups (nitro-PAHs) have been proven to be carcinogenic. Chapter 3 provides the first report on the electroanalysis of nitro-PAHs using chemically modified electrodes. A representative nitro-PAH species, namely nitropyrene were readily extracted onto electrochemically pretreated glassy carbon electrodes (PGCE) from methanol solutions. Nitropyrene species adsorbed on PGCE were reduced electrochemically to aminopyrene in a 6-electron process in 0.5 M H_2SO_4 solution. Experimental results showed that the peak current resulted from nitropyrene reduction was proportional to the concentration in their

methanol solution for a wide range of 1~1500 ng/mL with a large slope of 0.0864 A L g^{-1} and a correlation coefficient of 0.999. The preconcentration and determination conditions, as well as possible interference from other PAH species, were investigated. Possible application in determination of nitropyrene in air particulate was evaluated.

Silver ions were found to be readily incorporated onto polypyrrole films without deliberate incorporation of chemically active counterions. In chapter 4, the preconcentration and determination of the silver species at polypyrrole film electrode was studied in detail. The effects of PPy film coverage and preparation conditions, redox states of PPy, solution composition, pH and the presence of other metal ions have been investigated. Experimental results showed that the peak current gave good concentration dependence in the range of 2 ~ 150 μM. The detection limit was about 0.2 μM (20 ppb). Most of the metal ions studied including cobalt, nickel, cadmium, lead, zinc and iron did not show obvious interference on the determination. Mercury species were also incorporated on PPy film electrodes and influenced significantly the silver response. The mechanism involved in the preconcentration of silver species at PPy film electrodes was proposed.

In addition to the voltammetric response, the potentiometric response performance of PPy films with different thickness has been studied and reported in chapter 5. The morphology and electrochemical behaviors of the PPy films with different thickness were examined. The thick PPy film (> 3 μm) electrode showed a mixed potentiometric response for the anionic and cationic species present in the contacting solution. However, the results indicated that the thin PPy film electrodes (< 2 μm) always showed good pH response in the range of pH 2-12 with a slope of about -50 mV/pH, independent of the composition of the conditioning and test solutions. Acid-base equilibrium of the thin PPy film was involved and the potentiometric responses to pH change were related to the protonation and deprotonation of the nitrogen atoms present in the PPy chains. Different response mechanisms were involved in the potentiometric response for the thick and thin PPy film electrodes.

TABLE OF CONTENTS