Direct separation of faradaic and double layer charging current in potential step voltammetry

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ABSTRACT

Double layer charging current in electrochemical systems has been a challenging problem in the last several decades because it causes interference to the accurate measurement of faradaic current. A method for extracting faradaic current and double layer charging current directly from the measured total current in potential step voltammetry is developed by using iterative target transformation factor analysis (ITTFA). The method constructs initial target vectors based on the theoretical formulae of faradaic and charging current, and then calculates the weights of faradaic and charging current in the measured signal via the iterative transformation of the initial vectors. Therefore, the two currents in one experiment can be obtained simultaneously without any assumption. The potential step voltammetric signals of potassium ferricyanide, copper sulfate and paracetamol were analyzed with the proposed method. The results show that the shape of the obtained voltammogram is an ideal sigmoid curve with horizontal straight baseline and plateaus, and the intensity of the signal is greatly enhanced. Therefore, the method provides a new way to measure the pure faradic current in the potential step voltammetric experiment, and may provide an alternative for improving the sensitivity of quantitative analysis.

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1. Introduction

How to separate faradaic current from double layer charging current in an electrochemical system that has been a challenge in the last several decades [1–3]. Double layer charging current, which is generated with the change of potential on the working electrode surface, causes interference to faradaic current and restricts the detection limit and accuracy of the measurement [4]. Most of the work has been focused on minimizing the contribution of charging current to total current signal [5,6]. Many efforts have been made to improve the experimental instrument or signal pattern for increasing faradaic to charging current ratio, such as circuitry design [7], duplicate electrolysis cells [8,9], microelectrode [10,11], sinusoidal voltammetry and staircase voltammetry [12–15], etc. However, the difference between reference and sample, and the difficulty of parameter selection may lead to incorrect or incomplete elimination of charging current.

Chemometrics has speeded up the development of electrochemical analysis [16–23]. With the aid of chemometric methods, such as curve-fitting [24,25], Kalman filter [26], derivative techniques [27], Fourier transform [28–31], mathematical processing techniques for improving the faradaic to charging current ratio

becomes viable. Based on the differences between faradaic and charging current, interference of charging current can be eliminated by means of mathematical processing. However, it is still difficult to clearly know the absolute values and variation trend of charging current in an electrochemistry system. Besides, there have been methods for separating faradaic current from charging current with the assumptions of electrode process, such as the method based on electrochemical impedance spectroscopy [32], a posteriori or a priori separation [33–36]. These methods are based on certain assumptions and need to simultaneously determine several proper circuit or experimental parameters. Nevertheless, it is not an easy task to determine the accurate value of the parameters. The number of the parameters can be reduced if additional assumptions about the double layer model are introduced. This, however, makes the problem more complex.

In this paper, a method is presented to directly separate faradaic current from double layer charging current in potential step voltammetry via iterative target transformation factor analysis (ITTFA). ITTFA has been successfully applied in determination of a specific component in mixtures by means of an iterative transformation of a target vector representing the character of the component [37,38]. The core idea of the method is to iteratively transform the initial target vector to obtain the weight (concentration) of the component in an overlapping signal. In this study, the initial target vectors are constructed based on faradaic or charging decaying current formula, and then the weight of the faradaic and double layer charging current can be calculated with

the iterative transofrmation. Therefore, the approach can simultaneously obtain the faradaic and charging current, respectively, from the measured current in one experiment without any assumption.

2. Experimental

2.1. Chemical reagents

All chemical reagents used were of analytical grade except paracetamol of chemical grade. A further purification will be better for obtaining more precise measurements; these reagents were directly used to make the proposed method more practical. Potassium ferricyanide (99.5%), potassium nitrate (99%), copper sulfate (99%), anhydrous sodium sulfate (99%), paracetamol (98%) and hydrochloric acid were purchased from Guangfu Chemical Co., Ltd. (Tianjin, China). Potassium ferricyanide, copper sulfate and paracetamol solutions were prepared with 0.5 M potassium nitrate, 0.1 M sodium sulfate and 0.2 M hydrochloric acid, respectively. Doubly distilled water was used in preparation of the samples.

2.2. Instrumentation and procedures

A self-made electrochemical workstation was used, consisting of a data acquisition card (NI USB-6211, National Instruments Corporation, Texas, USA), potentiostat circuit board (Lanlike Chemistry & Electron High Technology Co., Ltd., Tianjin, China) and personal computer (Lenovo, Beijing, China). The programs were written in MATLAB (The MathWorks Inc., USA). Three electrode system made up of a 3 mm-diameter bare glassy carbon electrode (working electrode), a saturated calomel electrode (reference electrode) and a platinum sheet electrode (auxiliary electrode) was used for all the measurements. All potentials reported were referred to the saturated calomel electrode (SCE). Different electrode systems can be used for investigation of the proposed method, the commonly used electrode system, however, was used for generalization.

In the potential step experiments, normal pulse voltammetry was used, i.e., the potential form is consisted of a series of pulses, and each pulse increases to a potential and returns to the initial value. A pulse width of 60 ms and interval of 1.0 s between successive pulses were employed. Sampling rate is 20,000 points per second. For potassium ferricyanide, the potential was scanned in the range from 0.6 to −0.2 V with an increment of −0.02 V. For copper sulfate and paracetamol, the potential ranges 0.4 to −0.4 V and 1.1 to 0.3 V, increased by −0.02 V, were used. All solutions were carefully degassed with high-purity nitrogen for 5 min prior to the measurements in order to remove oxygen. All the experiments were carried out at room temperature (ca. 25 °C).

3. Theory and calculations

3.1. Basic idea

In potential step voltammetry, the measured current is a total of faradaic and charging current. The former decays in accordance with squared root of time, while the latter decays exponentially with time. The separation of the two currents can be realized based on the different decaying rates. The idea of the proposed method is to construct the initial target vectors based on the theoretical formula of the two currents and then to calculate the weights of them in the measured signal. Finally the two currents in an electrochemical system can be obtained by multiplying the final target vector and the loading (weights) vector. Therefore, the

approach can simultaneously calculate the faradaic current and charging current, respectively, from the measured current data in one experiment without any assumption.

3.2. Iterative target transformation factor analysis (ITTFA)

The basic model for an analytical signal of multicomponent system can be written as,

$$\mathbf{D} = \mathbf{S}\mathbf{C}^T \tag{1}$$

where $\mathbf{D}$ denotes the measured signal, $\mathbf{S}$ represents the pure or standard signal of the components and $\mathbf{C}$ means the concentration (relative to the standards) of the components. In this study, $\mathbf{S}$ is composed of two vectors representing the faradic and changing current, respectively, and $\mathbf{C}$ means the relative weights of the two currents in the measured total current. The superscript T means the transposition operation.

The aim of ITTFA is to calculate $\mathbf{S}$ and $\mathbf{C}$ from a measured $\mathbf{D}$ with an initial target vector constructed with estimations of the components. To achieve the purpose, principal component analysis (PCA) can be performed to obtain a score matrix $\mathbf{R}$, a loading matrix $\mathbf{V}$, and the eigenvalues λ of the matrix $\mathbf{D}$.

$$\mathbf{D} = \mathbf{R}\mathbf{V}^T \tag{2}$$

Mathematically, the vectors in loading matrix are combinations of the vectors in $\mathbf{C}$, and the score matrix corresponds to the weights of the combination. Therefore, $\mathbf{R}$ and $\mathbf{V}$ can be converted to $\mathbf{S}$ and $\mathbf{C}$ by mathematical transformation. If a target vector $\overline{\mathbf{R}}_l$ is provided, a transformation matrix or projection matrix $\mathbf{T}_l$ can be obtained to transform $\mathbf{R}$ to $\mathbf{S}$.

$$\mathbf{T}_l = \lambda^{-1}\mathbf{R}^T\overline{\mathbf{R}}_l \tag{3}$$

$$\mathbf{S}_l = \mathbf{R}\mathbf{T}_l = \mathbf{R}\lambda^{-1}\mathbf{R}^T\overline{\mathbf{R}}_l \tag{4}$$

Defining $\quad \mathbf{P} = \mathbf{R}\lambda^{-1}\mathbf{R}^T$

$$\mathbf{S}_l = \mathbf{P}\overline{\mathbf{R}}_l \tag{5}$$

Furthermore, when the values in $\overline{\mathbf{R}}_l$ are not exactly correct, corrections of these values can be obtained by iteratively replacing the values in $\overline{\mathbf{R}}_l$ with the values in the calculated $\mathbf{S}_l$. Therefore, the calculation of ITTFA can be summarized as [38],

(1). Perform PCA to the data matrix $\mathbf{D}$, obtaining $\mathbf{R}$ and λ.
(2). Construct an initial iterative target vector $\overline{\mathbf{R}}_l$, and calculate $\mathbf{T}_l$ and $\mathbf{P}$ matrix using Eqs. (3) and (4).
(3). Calculate $\mathbf{S}_l$ using Eq. (5) iteratively by replaceing $\overline{\mathbf{R}}_l$ by $\mathbf{S}_l$ until $\overline{\mathbf{R}}_l$ does not change.

3.3. Direct separation of faradic and charging current by ITTFA

The idea of the proposed method is to construct the initial target vectors using faradaic or charging current formula and then to achieve the separation using ITTFA. The following steps are included in the calculations:

(1). Prepare the decaying current matrix ($\mathbf{D}$): The decaying current of each potential step is measured and the matrix $\mathbf{D}_{n \times m}$ is constructed by aligning the decaying current at each pulse, where n denotes the data point number sampled in a pulse and m denotes the number of pulses at different potentials.
(2). Construct the initial iterative target vectors using Eqs. (6) and (7), respectively.

$$i_f = f(E)t^{-1/2} \tag{6}$$