J. Flow Injection Anal., Vol. 8, No. 1 (1991)

# Coulo-amperometric cell with spherical carbon felt electrode for flow injection analysis

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## Abstract

A novel electrochemical detection having multi-function of both amperometric and coulometric cells has been fabricated for the continuous analysis of electroactive species. This cell has been constructed in a concentric configuration, by rolling an ion exchange membrane and a counter carbon felt around the spherical working carbon felt electrode. The sample solution added into the working electrode is coming out from the bottom of the carbon felt by a gravity, undergoing the complete electrolysis with more than 98 % current efficiency. The peak current value is in proportional to the concentration of electro-active species in the sample solution, and the present cell is expected to be useful device in a flow injection system.

## Introduction

Controlled potential coulometry has been developed for the effective determination method of a variety of compounds[1,2]. In general, a coulometric cell can be divided two categories, that is, batch and flow types, and a conventional batch type cell need a rotation or a vibration of electrolyte in order to shorten the electrolysis time. On the the hand, a carbon felt electrode has been found to be very effective material in batch[3-10] and flow coulometric cells, in the respect that the rapid complete electrolysis can be performed within 10-20 seconds without a rotation or a vibration of the electrode and electrolyte. However, in this method, the number of the rapid electrolysis by a repetitive sample addition is limited because the added sample solution is stayed at the working carbon felt, consequently, the diffusion rate of sample solution becomes slow according to increase of number of the sample addition.

The peak current value is dependent on the extent of the dip of the carbon felt surface. Therefore, amperometric determination with a high precision been difficult to be carried out by the coulometric cell using a carbon felt electrode. But if the added solution is removed from the bottom of the carbon felt electrode by gravity, the peak current fluctuation caused by the variation of the extent of the dip should be minimized and the peak current would be proportional to the concentration of the added sample solution. An electrolytic cell which is able to use in not only coulometry but also amperometry is provided.

In this work, we now intend to describe a novel coulometric cell which can give the peak current proportioning to the concentration of the added electroactive species, and this electrochemical device was named as a coulo-amperometric cell.

This electrolytic cell has the structure that an ion exchange membrane and a counter carbon felt are surrounded around the spherical working carbon felt electrode. The determination of ferrocyanide ion, ferricyanide ion and dl-epinephrine were chosen to estimate the function of the present cell and the amperometric and coulometric response characteristics of these electro-active species have been described.

## Experimental

The apparatus used in this experiment were described earlier[3)] and a micropipet with variable volume is used to add the sample solution. The cross section of the electrolytic cell is shown in Fig. 1. The fabrication procedure of this cell is

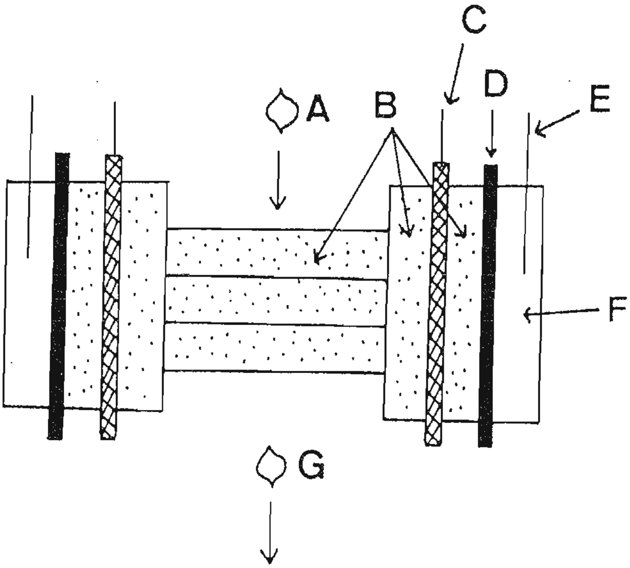

Fig. 1 Cross section of the coulo-amperometric cell
A: sample solution drop, B: working carbon felt electrode, C: platinum net for electrical contact, D: ion exchange membrane, E: Pt lead, F: counter carbon felt electrode, G: solution drop coming out from carbon felt.

described as follows. First, three round carbon felts (3 mm of thickness, id, 38 mm) dipped by electrolyte were piled up in the cylindrical platinum net. The platinum net with symmetry to the center axis was selected to diminish the potential distribution of the carbon felt. Next, The same carbon felt(50 x 150 mm) was wound around the platinum net and the ion exchange membrane was rolled outside this carbon felt. Finally, The counter carbon felt(50 x 150 mm) was wound around the ion exchange membrane and was used as a counter electrode. As an electrolytic solution, acetate buffer solution(pH 3.0) was used throughout the experiment. As counter solutions, saturated ferricyanide ion and ferrocyanide ion(pH 3.0, 1 M acetate buffer) were used when electrooxidation and electroreduction were carried out at a working electrode, respectively. The volume of electrolyte and a counter solution contained in the carbon felts were about 15 ml and 8 ml, respectively. The standard solutions of ferrocyanide, ferricyanide ions and dl-epinephrine were prepared by dissolving reagent grade potassium ferrocyanide, potassium ferricyanide and dl-epinephrine into distilled water.

The experimental procedure is as follows. First, the potential of the working electrode was maintained at a constant value. After the background current was reached to the steady-state value(about 1 mA), this current was compensated to zero by a bias circuit in a coulometer. Next, the repetitive addition of the sample solution were carried out by a micropipet(Eppendorf varipipet, 1-100 $\mu$l) with constant time interval.

The current vs time curves were recorded and the total charge consumed by the electrode reaction was obtained with a coulometer. The relationship between the concentration and peak current value or the current efficiencies were obtained.

## Results and discussion

When a platinum wire(0.5 mm diameter) was used as a electric lead of the working electrode in place of a platinum net, the charges and the current response were significantly varied by the dropping point of sample solution because the potential of the working electrode has a large potential distribution. It is then essential for the accurate and rapid electrolysis to use a cylindrical platinum gauze as an electric contact.

Effect of the concentration of the added ferrocyanide ion on the current peak shape is shown in Fig. 2. This result indicates that the peak current is increased in proportion to the concentration of ferrocyanide ion and the peak current was returned to a original baseline within 30 seconds even if the repetitive addition of the sample was carried out.

The peak currents and charges obtained by the addition of each sample solution volume are shown in Table 1. These results indicate that the current efficiencies are more than 98 % and the peak current value is increased in proportion to the sample solution volume. Therefore, it can be recognized that the current efficiency and a linearity of the peak current with sample volume are not influenced by the sample volume up to 30 μl. But, the peak current does not increase in proportion to the volume in the range more than 40 μl, although the current efficiency is not

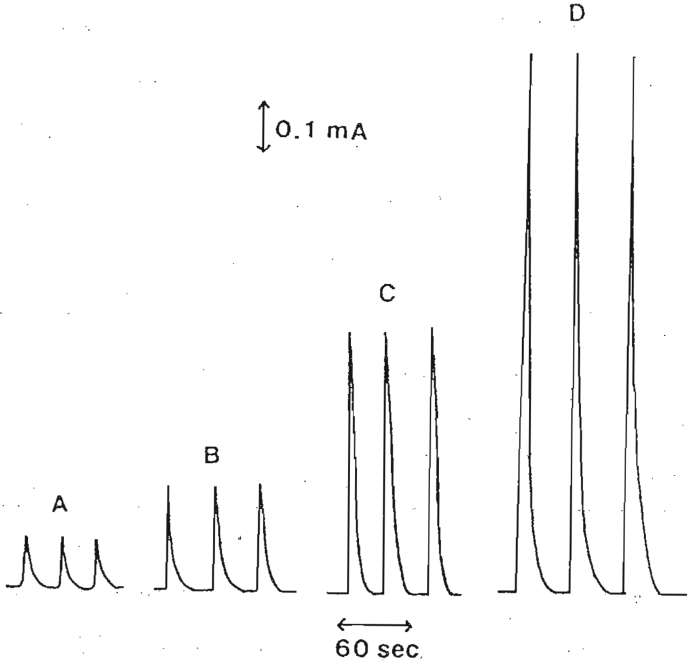

Fig. 2 Current vs time curves obtained by the repetitive addition of each concentration of ferrocyanide ion(10μl). A:1 x $10^{-3}$ M, B: 2 x $10^{-3}$ M, C: 5 x $10^{-3}$ M, D:1 x$10^{-2}$ M.

Table 1. Results of charges and peak currents of 1 x $10^{-2}$M ferrocyanide ion at each sample solution volume.

| volume (μl) | charge (mC) | RSD (%) | CE (%) | peak current (mA) | RSD (%) |
|---|---|---|---|---|---|
| 5 | 4.75 | 0.7 | 98.5 | 0.53 | 1.2 |
| 10 | 9.50 | 0.4 | 98.5 | 1.08 | 1.3 |
| 15 | 14.32 | 0.3 | 99.0 | 1.51 | 0.9 |
| 20 | 19.03 | 0.2 | 98.6 | 2.04 | 0.7 |
| 30 | 28.74 | 0.2 | 99.3 | 3.08 | 0.7 |

RSD: relative standard deviation, CE: current efficiency decreased. It can be considered that this fact is mainly due to the fluctuation of the shape of sample solution drop from micropipet operated manually when the sample volume becomes large value.

It can be easily considered that current efficiency is dependent on the thickness of the working carbon felt, that is, number of the carbon felts piled up. The current efficiencies were below 98% when one or two carbon felts were piled up, the electrolytic cell equipped with three carbon felts could then be useful as a controlled potential coulometric cell in which the sample is completely electrolyzed during passing through the electrode.

The analytical results obtained by amperometry and coulometry using the present electrolytic cell are shown in Table 2. The relative standard deviations of the peak currents and the charges are found to be less than 2 % and 1 %, respectively, and it was

Table 2. Coulometric results of ferricyanide ion , ferrocyanide ion and dl-epinephrine

| analyte | concn. ($\times 10^{-3}$M) | amperometry current (mA) | amperometry RSD (%) | coulometry charge (mC) | coulometry CE (%) | coulometry RSD (%) |
|---|---|---|---|---|---|---|
| ferricyanide ion | 1.00 | 0.123 | 1.4 | 0.960 | 99.5 | 0.6 |
| | 0.80 | 0.098 | 1.6 | 0.768 | 99.5 | 0.4 |
| | 0.50 | 0.060 | 2.0 | 0.480 | 99.5 | 0.8 |
| ferrocyanide ion | 10.0 | 1.198 | 0.5 | 9.550 | 99.0 | 0.7 |
| | 5.0 | 0.601 | 1.4 | 4.770 | 98.9 | 0.9 |
| | 1.0 | 0.120 | 1.1 | 0.953 | 98.8 | 0.6 |
| dl-epinephrine | 1.0 | 4.09 | 1.7 | 3.800 | 98.4 | 0.8 |
| | 0.5 | 1.97 | 1.2 | 1.900 | 98.4 | 1.8 |
| | 0.1 | 0.40 | 2.0 | 0.379 | 98.2 | 0.9 |

sample volume: 0.01 ml, CE: current efficiency, RSD: relative standard deviation.

estimated that an amperometric determination can be performed as well as coulometry using this electrolytic cell.

The current vs time curves obtained by the repetitive addition with each time interval of the sample addition is shown in Fig. 3. When the time intervals are 5 ,10 and 15 seconds, the sample solution was added before the previous sample is not electrolyzed completely yet and the electrolytic current continues to increase until the electrolytic current becomes constant. The reason why the electrolytic current becomes constant is that the amount of the charge decreased by an electrolysis corresponds to that of the charges increased by the addition. On the other hand, when the time interval is 20 seconds, the electrolytic current is decreased to the original

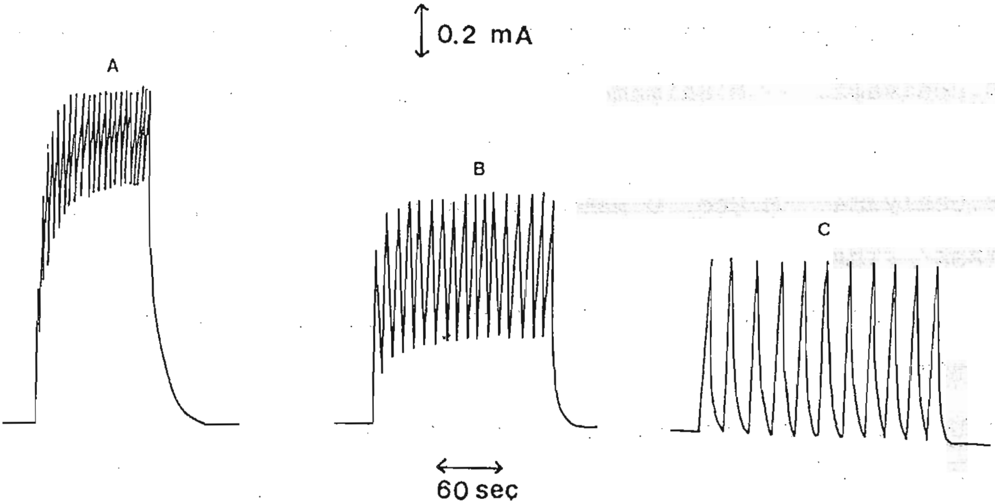

Fig. 3 Effect of the time interval of the repetitive sample addition of 5 x $10^{-3}$ M ferrocyanide ion(10 $\mu$l) on the shape of the current vs time curves.
time interval: A: 5 s, B: 10 s, C: 20 s.

baseline completely each time. This fact indicates that the time interval is very important factor when the present cell is applied to the coulometric or amperometric detector in a flow system.

From the results and discussion described above, the present electrolytic cell has an effective merit that the repetitive addition can be performed continuously, because an excess of electrolyte increased by the sample addition is removed by gravity, and it can be expected that this device would be useful one as a novel electrochemical detector in a flow injection method and liquid chromatography.

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(Accepted 25 May, 1991)