



Precise coulometric determination of redox inert anions based on electrolysis at the aqueous|organic solution interface

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ABSTRACT

The flow cell proposed previously for the rapid and coulometric determination of cations based on the electrochemical ion transfer at the aqueous|organic solution interface was improved to be applicable to the determination of anions. The developed cell was composed of a porous poly(tetrafluoroethylene) tube (1.0 mm in inner diameter), a copper wire (0.8 mm in diameter) inserted into the tube, a platinum wire placed outside the tube, an organic solution into which the tube was immersed and a reference electrode in the organic solution. The aqueous solution containing a species of interest was flowed through the narrow gap between the tube and the copper wire. A potential difference was applied at the aqueous|organic solution interface by using the copper wire and the reference electrode in the organic solution in order to realize the ion transfer at the interface, and the current due to the interfacial ion transfer was detected by the copper and platinum wires. The developed cell was evaluated adopting the transfer of an anion such as perchlorate, picrate or alkylsulphonates from the aqueous solution to 1,2-dichloroethane (used as the organic solution), and demonstrated that the anions of 10^{-4} mol dm⁻³ level could be determined with coefficients of variations better than 0.2% ($n = 5$). The applicability of the developed cell to the flow injection analysis of anions was also discussed.

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1. Introduction

Coulometry is one of very important branches of analytical chemistry because of its unique advantage as an absolute method [1,2], and has been applied not only to the accurate and precise determination [3], but also to the identification of electrolysis products and elucidation of electrode processes [4–7]. Most of species determined by coulometry so far have been redox active since electrochemical principles applied to coulometric works have been redox reactions [1–7]. On the other hand, the present authors demonstrated [8–10] that even redox inert ions could be determined coulometrically with high accuracy and precision when the ion transfer reaction at the aqueous|organic solution, W|O, interface was adopted as another electrochemical principle. Here, Sawada et al. [11] also proposed a complete electrolysis method based on the ion transfer at the W|O interface, though the discussion from the view-point of the precise coulometric determination was not made.

In the coulometry developed by the present authors, a cell (see Fig. 1 in Ref. [8]) named as Flow Electrolysis Cell for Rapid Ion Transfer (abbreviated as FECRIT [9,10]) was used. The FECRIT was composed of a porous poly(tetrafluoroethylene), PTFE, tube (1.0 mm in inner diameter), a silver wire (0.8 mm in diameter) coated with silver chloride, Ag/AgCl wire, inserted into the tube, a platinum wire counter electrode placed outside the tube, O into which the tube was immersed and a reference electrode in O. The W containing a species of interest and a supporting electrolyte, SE, was forced to flow through the narrow gap (W-path) between the tube and the Ag/AgCl wire. The potential difference between W and O, E , was applied by using the Ag/AgCl wire and the reference electrode in O, and the current due to the interfacial ion transfer, I , was detected by the Ag/AgCl wire and platinum wire. Here, the Ag/AgCl wire worked as both reference and counter electrodes in W. A fairly concentrated salt of Cl⁻ was added to W as the SE in order to depolarize the interface between Ag/AgCl wire and W by the redox reaction of Eq. (1), and to keep the variation of E at the W|O interface negligible even under the current flow.



The FECRIT was successfully applied to the coulometric determination of cations such as K⁺, Ca²⁺ and Mg²⁺ even though they were redox inert. The determination was performed with accuracies and

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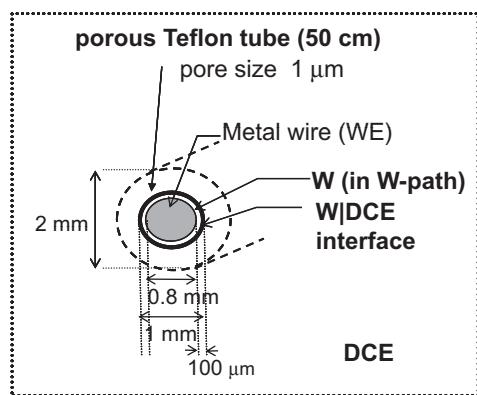


Fig. 1. Sectional view of the porous PTFE tube equipped with a metal wire used for the preparation of FECRIT (Flow Electrolysis Cell for Rapid Ion Transfer).

precisions of 99.7–100.3 and $\pm 0.1\%$, when concentrations of cations were 10^{-4} M ($M = \text{mol dm}^{-3}$) level ($n = 5$) [8,9]. The interference in the determination caused by diverse ions was removed by adopting a two-step FECRIT system in which the first one was used to remove the diverse ions and the second one to determine the ion of interest [9]. The electrochemical solvent extraction of actinide ions was also attained by using the FECRIT [10].

The FECRIT is useful for the coulometric determination of cations that transfer from W to O at relatively positive E (measured as the potential of W versus that of O) as described above. However, the determination of ions that transfer at negative E is difficult since the negative side of the potential window is narrow due to the transfer of Cl^- added as the SE anion in W. Here, the potential window means the E region limited by the large positive and negative currents due to the transfers of SE ions (called as the final rise and the final descent, respectively). In order to expand the negative side of the potential window, it is necessary to exchange Cl^- (the SE anion) that is not hydrophilic enough for a fairly hydrophilic anion such as SO_4^{2-} .

In the present work, a new FECRIT system was developed by using Cu wire instead of Ag/AgCl wire and CuSO_4 as SE in W. The Cu wire|W interface was depolarized based on the Cu^{2+}/Cu redox

reaction. The potential window was expanded dramatically, and the coulometric determination of anions such as perchlorate, picrate and alkylsulphonates could be performed by using the new FECRIT system. The optimal conditions for the determination were investigated.

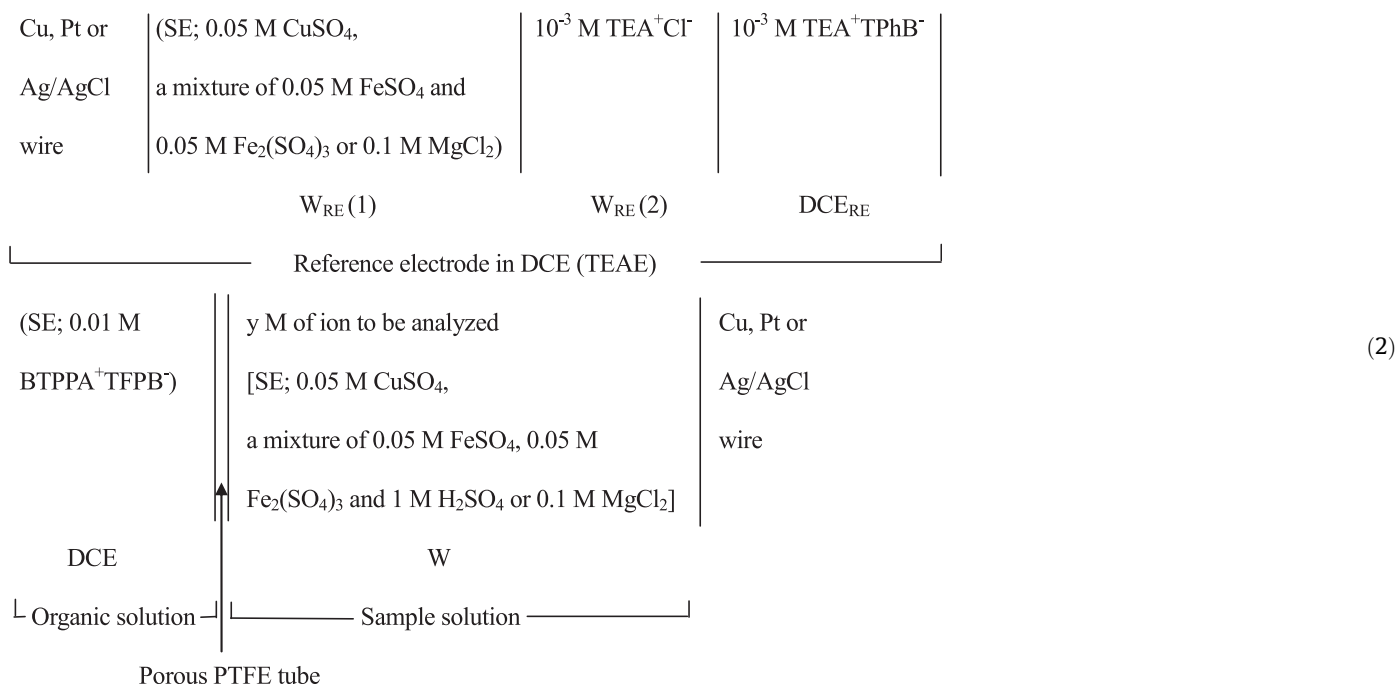
2. Experimental

2.1. Fabrication of FECRIT and procedure for electrolysis

The FECRIT system investigated was essentially identical to that described in previous papers [8–10] except for the metal wire inserted into the porous PTFE tube and the SE added in W (see Fig. 1). A wire of Cu or Pt was examined in place of Ag/AgCl wire that was used in previous works. The porous PTFE tube (PoreflonTM tube, TB-0201; a product of Sumitomo Electric Fine Polymer Inc.) was $1 \mu\text{m}$ in pore size and 60% in pore density. The O employed was 1,2-dichloroethane, DCE.

The tube with the inserted metal wire was pretreated before its use as follows; (I) the tube was washed by passing distilled water through the W-path at a flow rate of W , f , of 0.5 mL min^{-1} for 5 min. Then, (II) immersed in ethanol and washed for 10 min under an ultrasonic vibration. Finally, (III) the similar ultrasonic cleaning was carried out in DCE instead of ethanol.

The pretreated tube with the metal wire was immersed in DCE containing 0.01 M bis(triphenylphosphoranylidene)ammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, $\text{BTPPA}^+\text{TFPB}^-$, as SE. Electrolysis was performed by forcing W containing a species of interest and SE to flow at a constant f (0.1 mL min^{-1} , unless otherwise described), through the W-path with the aid of a syringe pump (Model 210, KD Scientific Inc.). The SE added in W was CuSO_4 or a mixture of FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$, when the metal wire was Cu or Pt, respectively, in order to depolarize the W|metal wire interface based on Cu^{2+}/Cu or $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox reaction, respectively. The FECRIT composed of Ag/AgCl wire was also examined by using W containing 0.1 M MgCl_2 as the SE. The W|DCE interface was formed at the inner surface of the tube since the tube is hydrophobic. The cell configuration of the FECRIT system can be described as Eq. (2).



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