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Development of high performance electrochemical solvent extraction method

Tomohiko Okugaki [a], Yoshihiro Kitatsuji [b], Megumi Kasuno [c], Asuka Yoshizumi [a], Hiroki Kubota [a], Yayoi Shibafuji [a], Kohji Maeda [a], Zenko Yoshida [d], Sorin Kihara [e,*]

[a] Department of Chemistry, Kyoto Institute of Technology, Sakyo, Kyoto 606-8585, Japan
[b] Nuclear Science and Engineering Directorate, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan
[c] Department of Materials Chemistry, Faculty of Science and Technology, Ryukoku University, Seta, Otsu 520-2194, Japan
[d] Nuclear Science Research Institute, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan
[e] Department of Natural Sciences, Faculty of Education, Kumamoto University, Kurokami, Kumamoto 860-8555, Japan

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ABSTRACT

A high performance electrochemical solvent extraction method was developed based on the quantitative transfer of ions from an aqueous, W, to an organic solution, O. It was realized by applying a potential difference, *E*, between W and O. The electrolytic cell used was similar to that reported for the rapid and coulometric ion transfer at the W/O solution interface. The cell was composed of a porous Teflon tube (with a 1.0 mm inner diameter and 50 cm length), a silver wire (0.8 mm diameter) inserted into the tube, a platinum wire placed outside the tube, O where the tube was immersed and a reference electrode, RE, in the O. When W containing ions was forced to flow through the narrow gap between the tube and silver wire, and *E* was applied by using the silver wire and RE, a very rapid quantitative ion transfer was attained. For example, when 1,2-dichloroethane containing bis(diphenylphosphinyl)ethane, BDPPE, was used as O, more than 99% of the UO_2^{2+} in W was extracted during the residence (e.g., 40 s) of W in the cell. The fundamental feature of the extraction system was investigated, taking into account the application of the system to the extraction of actinide, lanthanide, Sr or Cs ions. In order to facilitate the ion transfer, BDPPE, bis(diphenylphosphinyl)methane or dibenzo-18-crown-6 was added to O. The use of a column electrode system connected before the extraction system was examined in order to adjust the oxidation state of the element to that desired.

1. Introduction

Solvent extraction is a useful and widely applied separation method. Hence, investigations to develop high performance extraction systems, selective extraction reagents and novel solvents have been actively conducted to improve the separation efficiency, preserve the environment, decrease cost, etc. [1–8].

One of the new solvent extraction techniques for which wide practical application is expected is a technique that has been called 'electrochemical extraction', 'electro-assisted solvent extraction', 'electrochemical solvent extraction', 'electrochemically assisted solvent extraction' or 'electrochemically modulated solvent extraction' [9–14]. The term 'electrochemical solvent extraction' will be adopted for use in this paper. In electrochemical solvent extraction, ion transfer at the aqueous/organic solution, W/O, interface is realized by applying a potential difference, *E*, between W and O.

The theoretical grounds of the electrochemical solvent extraction method rely heavily on the fruits of voltammetry for ion transfer at the interface between two immiscible electrolyte solutions (VITIES). The transfer free energies and transfer processes of ions of various chemical properties at the W/O interface, complex formations of ions with ionophores in O, rates of ion transfer, etc. have been investigated widely based on VITIES during the last few decades [15–20]. The measurement of capacitance or impedance at the interface, together with VITIES, has offered information on the rate and mechanism of the ion transfer [12,16,21–24]. VITIES has also been applied to the elucidation of the processes involved in solvent extraction, as well as membrane transport [9,25–29]. In order to ascertain the ion transfer process at the W/O interface responsible for the voltammetric wave, controlled potential difference electrolysis was carried out by applying a definite potential difference, *E*, between W and O, and the species transferred was determined or identified [30,31].

The results of VITIES and controlled potential difference electrolysis suggest that, in principle, highly selective ion extraction could be performed by electrochemical solvent extraction, since *E* can be controlled precisely by using an outer electrolytic circuit, although electrochemical solvent extraction has not been widely used yet, especially in the field of practical analytical or separation chemistry.

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* Corresponding author. Tel./fax: +81 96 342 2541.
E-mail address: kiharas@educ.kumamoto-u.ac.jp (S. Kihara).

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The most serious barrier to the wide application of electrochemical solvent extraction is that it requires a fairly long time (e.g., 4 h) to attain a quantitative transfer of ions between W and O since the area of the W/O interface in an ordinary electrolytic cell is small compared with the volumes of W and O. This difficulty can be overcome by employing the flow electrolysis cell developed for rapid and coulometric ion transfer at the W/O solution interface [32]. Quantitative ion transfer was confirmed to be attained within 1 min by using this cell. Hereafter, this cell will be called the Flow Electrolysis Cell for Rapid Ion Transfer, abbreviated as FECRIT.

In the present work, the utility of the FECRIT in high performance electrochemical solvent extraction was examined by taking the mutual separation of ionic species related to spent nuclear fuel reprocessing or nuclear waste management as an example. An investigation was also made of the appropriate adjustment to attain the oxidation state of the element of interest for the extraction using a column electrode placed in front of the FECRIT. Here, the column electrode was an electrolytic cell that was useful for the rapid and quantitative redox reaction in a flow system [33,34].

2. Experimental

2.1. Chemicals

The O employed in the present work was 1,2-dichloroethane, DCE, purified according to the method described by Kadish and Anderson [35].

The capability of the FECRIT system was evaluated based on the transfer of Cs^+, Sr^{2+}, La^{3+}, Pu^{3+}, U^{4+}, Np^{4+}, Pu^{4+}, NpO_2^+, UO_2^{2+}, NpO_2^{2+} or PuO_2^{2+} at the interface between W and DCE, facilitated by an ionophore in DCE. The ionophores examined were bis(diphenylphosphinyl)ethane, BDPPE, bis(diphenylphosphinyl)methane, BDPPM, and dibenzo-18-crown-6 (Aldrich, No. 12926AO), DB18C6. The stock solution of Cs^+, Sr^{2+} or La^{3+} was obtained by weighing a reagent grade of CsCl (Aldrich, No. 450774), $SrCl_2$ (Aldrich, No. 439665) or $LaCl_3$ (Aldrich, No. 449830), respectively, after drying the salt by heating at about 500 °C for 4 h, and dissolving with triple distilled water.

Stock solutions of U or Np ions were prepared by dissolving uranium metal (JAERI-U4, natural isotopic abundance) or neptunium dioxide (CEA, Fontenay-aux-Roses, France, isotopic abundance of $^{237}Np = 100\%$), respectively, in concentrated nitric acid solution. Those of Pu ions were prepared by dissolving plutonium metal (NBS-949c, USA, isotopic abundance of $^{239}Pu = 97.40\%$; $^{240}Pu = 2.56\%$; $^{241}Pu = 0.031\%$) in 3 M (M = mol dm^{-3}) hydrochloric acid. Stock solutions of UO_2^{2+}, NpO_2^{2+} and PuO_2^{2+} were prepared by the following procedure. An aliquot of the solution containing U, Np or Pu was heated to almost dryness. The residue was dissolved in 5 M $HClO_4$ and heated to dryness with fuming. After repeating the $HClO_4$ fuming procedure three times, the residue was dissolved in 1 M HCl. The oxidation state of U, Np or Pu was adjusted to be hexavalent, producing UO_2^{2+}, NpO_2^{2+} or PuO_2^{2+} by the fuming. The solution of U^{4+}, NpO_2^+ or Pu^{3+} was prepared by reducing the UO_2^{2+}, NpO_2^{2+} or PuO_2^{2+} by controlled potential electrolysis with a column electrode system [34]. The solution of Np^{4+} or Pu^{4+} was prepared by using the two-step column electrode system as follows [34]. NpO_2^{2+} or PuO_2^{2+} was reduced to Np^{3+} or Pu^{3+} at the 1st column electrode, and then oxidized to Np^{4+} or Pu^{4+}, respectively, at the 2nd column electrode. The oxidation states of the prepared actinide ions were confirmed by UV–VIS spectroscopy [36,37].

The preparation and purification of BDPPE and BDPPM were carried out according to the procedures found in the literature [38,39]. For the purification of DB18C6, DB18C6 was dissolved in acetonitrile and recrystallized by adding water to the acetonitrile solution.

Bis(triphenylphosphoranylidene)ammonium tetrakis[3,5-bis-(trifluoromethyl)phenyl]borate, $BTPPA^+TFPB^-$, used as the supporting electrolyte, SE, in DCE was obtained as a precipitate by mixing a methanol solution of $BTPPA^+Cl^-$ (Aldrich, No. 223832) with a methanol solution of Na^+TFPB^-. Here, Na^+TFPB^- was synthesized according to the procedure described by Nishida et al. [40]. Tetraethylammonium tetraphenylborate, TEA^+TPhB^-, used in the preparation of the reference electrode was obtained as a precipitate by mixing a methanol solution of TEA^+Cl^- (Aldrich, No. 140023) with a methanol solution of Na^+TPhB^- (Aldrich, No. T25402). $BTPPA^+TFPB^-$ and TEA^+TPhB^- were purified by recrystallization based on the temperature dependence of the solubility of the salts in ethanol [41].

All of the other chemicals used were of reagent grade quality.

2.2. FECRIT and the procedure for the electrolysis

The FECRIT used for the electrochemical solvent extraction was essentially identical with that developed for rapid and coulometric ion transfer and presented in a previous paper [32] (see Fig. 1). The cell is composed of a porous Teflon tube (with a 1 μm pore size and 60% pore density; a product of Sumitomo Electric Fine Polymer Inc.), a silver wire coated with silver chloride (Ag/AgCl wire) inserted into the tube, a platinum wire (0.5 mm in diameter) placed outside and parallel to the tube and a tetraethylammonium ion selective electrode (TEAE). The Teflon tube used had an inner diameter of 1.0 mm, an outer diameter of 2.0 mm and a length of 50 cm, unless otherwise stated, and the Ag/AgCl wire was 0.8 mm in diameter. The tube with the Ag/AgCl wire was immersed in DCE containing an SE and a neutral ligand (BDPPE, BDPPM or DB18C6) that facilitated the ion transfer. The electrolysis was performed by forcing W containing a species of interest and the SE to flow at a definite flow-rate, *f*, through the narrow gap between the tube and the Ag/AgCl wire (which is hereafter called the W-path) with the aid of a syringe pump (Model 210, kd Scientific Inc.). Here, a Cl^- salt of Cs^+ or Mg^{2+} or HCl of rather high concentration (0.1 M) was adopted as the SE in W in order to depolarize the interface between W and the Ag/AgCl wire based on the Ag/AgCl redox

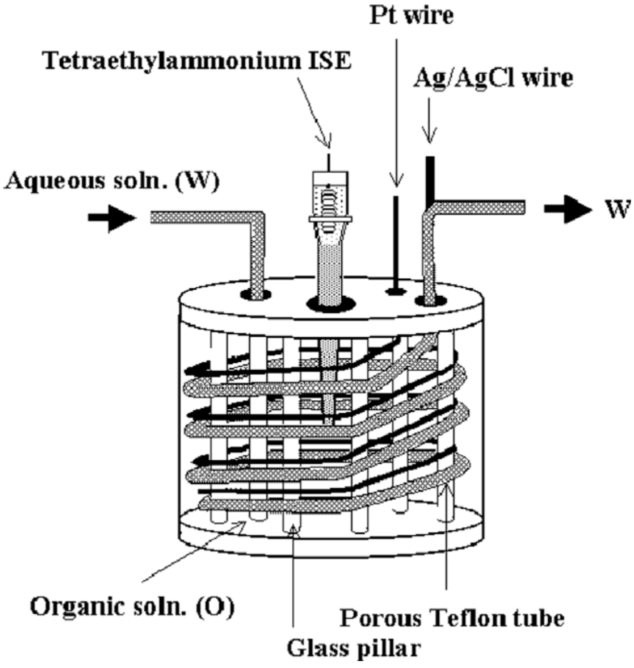

Fig. 1. Schematic illustration of the flow electrolysis cell for rapid ion transfer, FECRIT, used for the electrochemical solvent extraction.