



Electrochemical behavior of zirconium(IV) in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ionic liquid



G. Murali Krishna, A.S. Suneesh, K.A. Venkatesan*, M.P. Antony

Fuel Chemistry Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India

ARTICLE INFO

Article history:

Received 23 March 2016

Received in revised form 5 July 2016

Accepted 6 July 2016

Available online 07 July 2016

Keywords:

Room temperature ionic liquid

Zirconium

Voltammetry

Diffusion coefficient

Nucleation

Chronoamperometry

ABSTRACT

Zirconium is a constituent of metallic fuel in a nuclear reactor. The electrochemical behavior of Zr(IV) in the room temperature ionic liquid, 1-butyl-3-methyl imidazolium bis(trifluoromethylsulfonyl) imide ($C_4mimNTf_2$), was studied by various transient electrochemical techniques. The cyclic voltamogram of Zr(IV) in $C_4mimNTf_2$ consisted of a scant cathodic wave occurring at the potential of +0.2 V (Vs Pd), due to the reduction of Zr(IV) to Zr(II), and a prominent reduction occurring at the onset of -1.3 V (Vs Pd), due to Zr(II) to Zr(0). The metallic deposit was characterized by SEM-EDX and XRD analysis. A nucleation loop was observed at -1.6 V (Vs Pd). The cathodic peak current increased and marginally shifted cathodically with the increase of scan rate. The apparent diffusion coefficient of Zr(IV) in $C_4mimNTf_2$ was determined to be $10^{-10} \text{ cm}^2/\text{s}$ and a five-order increase in apparent diffusion coefficient ($10^{-5} \text{ cm}^2/\text{s}$) was observed with the onset of nucleation at -1.6 V (Vs Pd). The nucleation growth and decay of chronocurrent transient was fitted into instantaneous and progressive nucleation models. The nucleation phenomenon also altered the nature of chronopotentiogram of Zr(IV) with a drop from rest potential followed by increase in the potential of working electrode in the early part of the transient. The study indicated the possibility of electrodeposition of zirconium from $C_4mimNTf_2$ ionic liquid.

© 2016 Published by Elsevier B.V.

1. Introduction

The metallic zirconium exhibits excellent physicochemical and nuclear properties, finding several applications in the construction of nuclear components and nuclear reactor core elements [1,2]. Zirconium is being used as a cladding material for the nuclear fuel owing to its merits such as strong resistance toward corrosion, excellent mechanical properties, and poor thermal neutron cross section. In addition, zirconium is a constituent of the metallic fuel, which is composed of uranium–zirconium alloy or uranium–plutonium–zirconium alloy [3–5]. In these alloys, zirconium is generally present to the extent of 10 wt.%.

Non-aqueous pyrochemical electrorefining method has been proposed for reprocessing of spent metallic fuels [6–8]. In this method, the actinides present in the spent metallic fuel are anodically dissolved in the eutectic of high-temperature molten salt medium composed of LiCl–KCl and the dissolved actinides are recovered at cathode by electro-deposition. The details of metallic fuel electrorefining are described elsewhere [9,10]. It is important to recognize that this process usually

operates at temperatures at 773 K or above, depending upon the composition of chosen electrolyte. The dissolution of metallic fuel elements in molten salt medium is governed by the standard reduction potentials. The standard potential of Zr(IV)/Zr couple is reported to be more positive than the U(III)/U and Pu(III)/Pu reduction potential in LiCl–KCl melts [11,12]. This indicates that zirconium should not dissolve in the molten salt medium during anodic dissolution of uranium and plutonium from the spent metallic fuel. However, practical considerations of electrorefining method demand the operation of dissolution reaction at high current density for quantitative dissolution of actinides, especially at the end of dissolution. Under these constrained conditions, the potential of the anode is usually kept at much higher positive potentials, beyond the oxidation potentials of zirconium. Therefore, it is quite likely that a portion of zirconium also gets oxidized to Zr(IV) and dissolves in molten salt medium. In addition, due to the low negative potential needed for electrodeposition of zirconium, it is predominantly reduced to metallic form along with actinides during the recovery. Therefore, the presence of zirconium in the molten salt is usually considered as a nuisance.

In contrast to high-temperature molten salts, room temperature ionic liquids (RTILs) are organic salts molten at temperatures lower than 373 K [13,14]. Generally, they are made up of a bulky organic cation and an inorganic or organic anion. Employing such organic salts (or RTILs) in place of inorganic chloride media leads to the operation of

* Corresponding author.

E-mail address: kavenkat@igcar.gov.in (K.A. Venkatesan).

entire process at near ambient conditions. RTILs have several fascinating properties suitable for industrial exploitation [15–18]. The wide electrochemical window, usually >6 V, and extended cathodic stability makes RTILs, a promising candidates for non-aqueous reprocessing and nuclear fuel cycle applications [17,18]. In this context, several authors have investigated the spectroscopic, co-ordination, and electrochemical behavior of actinides in ammonium and imidazolium ionic liquid medium. It was reported that those ionic liquids offered wide electrochemical window and indicated the feasibility of reducing the actinides to metallic form. We also studied the suitability of using N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMPyNTf₂) ionic liquid for the electrodeposition of europium [19]. Extensive studies on the electrochemical behavior and electrodeposition of various metals on different substrates have been investigated by Endres and co-workers. Giridhar et al. studied the electrochemical behavior of niobium in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ([Py1,4]TfSA) ionic liquid [20]. The authors reported that niobium can be deposited in metallic form from pyrrolidinium ionic liquid. However, the deposit also contained some oxides of niobium. Borisenko et al. reported the electrodeposition of tantalum from ionic liquid medium containing TaF₅ and the deposition was monitored by EQCM [21]. Similarly, the electrodeposition of Nb and Cu from 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide was studied by Vacca et al. [22].

Metallic reactors use U–Pu–Zr-based alloy as fuel. Extensive studies have been reported in literature on the electrochemical behavior of individual metal ions such as U(III) and Zr(IV) as well as the combined behavior of U(III)–Zr(IV) in high-temperature molten salts [23,24]. However, the reports on the electrochemical behavior of these systems in room temperature ionic liquids are minimal. In the recent past, we reported [25] the voltammetric behavior of U(IV) in N-methyl-N-propylpiperidinium bis(trifluoromethylsulfonyl)imide (MPPiNTf₂) ionic liquid medium. The rate of dissolution of uranium oxide (UO₂) in HNTf₂ was studied at 353 K and the resultant U(NTf₂)₄ was dissolved in MPPiNTf₂ for studying the electrochemical behavior. The results revealed the possibility of depositing uranium in metallic form from MPPiNTf₂ ionic liquid. As far as zirconium is concerned, only little information is available in literature on the electrochemical behavior of Zr(IV) in ionic liquid medium. To the best of our knowledge, Tsuda et al. [26] reported the electrochemistry of Zr(IV) in aluminum chloride-1-ethyl-3-methylimidazolium chloride ionic liquid. However, this kind of ionic liquid is moisture and air sensitive. Fu et al. [27] reported the electrochemistry of zirconium tetrachloride in N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide. The authors reported the reduction of Zr(IV) to Zr(III) at platinum electrode. Further reduction of Zr(III) to metallic form or lower valence state was not observed. More recently Vacca et al. reported the electrochemical behavior of Zr(IV) in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulphonyl) imide ionic liquid, investigated by cyclic voltammetry and chronopotentiometry [28]. It was reported that Zr(IV) undergoes a two-step, two-electron transfer reduction reaction to metallic zirconium on various substrates. However, the diffusion coefficients, electron transfer kinetics, nucleation phenomenon, and chronoamperometry were not reported.

In view of the paucity of data on the electrochemical behavior of Zr(IV) in ionic liquid medium and toward the development of ionic liquids for metallic fuel reprocessing, the primary objective of the present paper is to report electrochemical behavior of Zr(IV) present in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (C₄mimNTf₂) ionic liquid medium. The electrochemical behavior of Zr(IV) was investigated by transient electrochemical techniques such as cyclic voltammetry, chronoamperometry, and chronopotentiometry. Since the mass transport of the analyte to the electrode surface occurs by diffusion, it is important to report the apparent diffusion coefficients of Zr(IV) in ionic liquid medium. Therefore, in this paper, we report the “apparent diffusion coefficient” of Zr(IV) and the electron transfer kinetics involved in the electrodeposition.

2. Experimental

2.1. Materials and reagents

All the chemical and reagents used in this study were analytical grade. 1-Methylimidazole was purchased from Fluka. Lithium bis(trifluoromethanesulfonyl)imide (99.8%) was procured from Sigma Aldrich. Anhydrous Zirconium (IV) chloride (99.9%) was procured from Sigma Aldrich. Palladium wires and Glassy carbon were purchased from Johnson Matthey. The ionic liquid, 1-butyl-3-methylimidazolium bis (trifluoromethanesulfonyl)imide (C₄mimNTf₂), was prepared by the procedure described elsewhere [25,29].

2.2. Sample preparation for SEM-EDX and XRD measurement

Sample for SEM-EDX and XRD measurement was prepared by electrodepositing zirconium metal on a glassy carbon substrate (cylindrical SA = 0.25 cm²) and Pd wire (cylindrical SA = 0.10 cm²) acted as counter and quasi-reference electrodes, respectively. A solution of Zr(IV) (30 mM) in C₄mimNTf₂ was prepared by dissolving anhydrous ZrCl₄ in C₄mimNTf₂, under constant stirring at room temperature. To obtain this deposit, electrolysis of Zr(IV) in C₄mimNTf₂ was carried out for about 1 hour at glassy carbon working electrode at –1.7 V (Vs Pd). The deposit was washed with moisture-free acetone and dried in air. The zirconium deposit present on the glassy carbon substrate was subjected to SEM-EDX analysis. For XRD measurements, the electrodeposited sample was removed and smeared on an aluminum sample holder before recording.

2.3. Instrumentation

Cyclic voltammogram Zr(IV) in ionic liquid medium was recorded using Autolab (PGSTAT-030) equipped with an IF 030 interface. A solution of Zr(IV) (30 mM) in C₄mimNTf₂ was prepared by dissolving anhydrous ZrCl₄ in C₄mimNTf₂, under constant stirring at room temperature. Voltammetric studies were carried out in a temperature range 353–383 K. A glassy carbon rod (cylindrical SA = 0.16 cm²) was used as working electrode. A glassy carbon rod (cylindrical SA = 0.25 cm²) and Pd wire (cylindrical SA = 0.10 cm²) acted as counter and quasi-reference electrodes, respectively. For open circuit potential measurements, zirconium metal rod (cylindrical SA = 0.32 cm²) was used as working electrode. The electrochemical cell had a single leak-tight compartment and all the electrodes were placed in the same compartment. The cell was kept under argon atmosphere during entire study. Electrodeposition was conducted on glassy carbon working electrode, with glassy carbon acted as counter electrode and palladium wire acted as quasi-reference electrode. After deposition, the electrode was washed extensively with acetone and deionized water before subjecting it for thermal analysis and surface morphology.

The X-ray diffraction pattern of the deposit was obtained using Philips 1011 X-ray diffractometer (operating with 40 KV and 45 mA) with Cu K α (1.5406 Å) radiation. Field emission gun-scanning electron microscopy (FEG-SEM) images were obtained using TESCAN MIRA 3 model at 15 kV. Energy dispersive X-ray spectral analysis (EDX) image was recorded with Oxford instrument to examine the surface morphology and elemental composition of the deposit.

3. Results and discussion

3.1. Cyclic voltammetry of Zr(IV) in C₄mimNTf₂

The ionic liquid medium requires a large electrochemical window and extended cathodic stability for the reduction of tetravalent zirconium to metallic form. The cyclic voltammogram of C₄mimNTf₂ recorded at glassy carbon working electrode at the scan rate 100 mV/s at 353 K is shown in Fig. 1. It can be seen that the cation reduction occurs at

Download English Version:

<https://daneshyari.com/en/article/217778>

Download Persian Version:

<https://daneshyari.com/article/217778>

[Daneshyari.com](https://daneshyari.com)