

Electrochemical behavior of UC in acidic media: Preliminary results

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Abstract

The electrochemical behavior of uranium monocarbide in 0.1–2 M HNO₃ and HClO₄ solutions was investigated, using linear voltammetry, multistep potential sweep coulometry and potential controlled electrolysis at the UC electrode. The electrochemical measurements indicated that the increase of the UC electrode potential caused the appearance of three ranges corresponding to slow, moderate and rapid oxidation of UC. The mechanism of oxidation processes at the UC/electrolyte interface were shown to change correspondingly. The potential boundaries separating the slow, moderate and rapid oxidation of UC were weakly affected by the acid concentration.

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1. Introduction

Uranium-based carbides have become a subject of renewed interest as possible fuels for future high-temperature gas-cooled reactors (HTGR) [1]. Since the minor actinides and most of the long-lived fission products (FP) could be incinerated in HTGRs, its reprocessing should be considerably simplified. In certain proposed aqueous flowsheets for HTGR fuel reprocessing the actinides (An) and FP would already be separated at the moment of fuel dissolution.

Numerous studies of UC dissolution in acid media have shown that the complete conversion of UC to soluble U(VI) was achieved in HNO₃ solutions exceeding 4 M [2]. However, uranium oxidation was accompanied by the accumulation of undefined organic species in the electrolyte [3,4]. Photochemical [5] and electrochemical [6] techniques were applied to oxidize the organic species to CO₂ and to accelerate UC dissolution. It is difficult to interpret the UC dissolution mechanism, however, due to the absence of fundamental data on UC electrochemical properties.

This preliminary study addresses UC electrochemical behavior in nitric acid media from 0.1 to 2 M. Because of the chemical and electrochemical inertness of ClO₄⁻ ions, perchloric acid solutions were also chosen as the working electrolytes for the present study. Linear voltammetry (LV) and multistep potential sweep coulometry (MPSC) were used as preliminary methods to determine the electrochemical properties of UC, and especially the potential boundaries characterizing the different rates of UC oxidation.

2. Experimental

Spherical UC ingots of about 3 mm diameter were prepared by arc melting of a stoichiometric mixture of graphite and uranium metal chips with an inert (W) electrode in a water-cooled copper crucible in argon atmosphere [7]. The UC microsphere was then pressed into a Teflon tip and connected to an EDI101T electrode assembly (Radiometer). This hemispherical electrode served as a working electrode in a three-electrode system also comprising an Hg/Hg₂Cl₂ reference electrode (SCE) and a Pt wire counter electrode under nitrogen atmosphere. For the LV measurements, the working electrode was used with a 5 mV/s polarization rate. MPSC experiments consisted in successive runs of potential controlled electrolyses (PCE) carried out, for 1 min each, under a potential increasing from the open circuit potential $E_{f=0}$ to 1.5 V/SCE by 50 mV steps. The current versus time curves were then integrated to obtain the charge passed through the cell as a function of the applied potential. LV and MPSC measurements were carried out using a PGZ 301 potentiostat with Voltalab 40 software.

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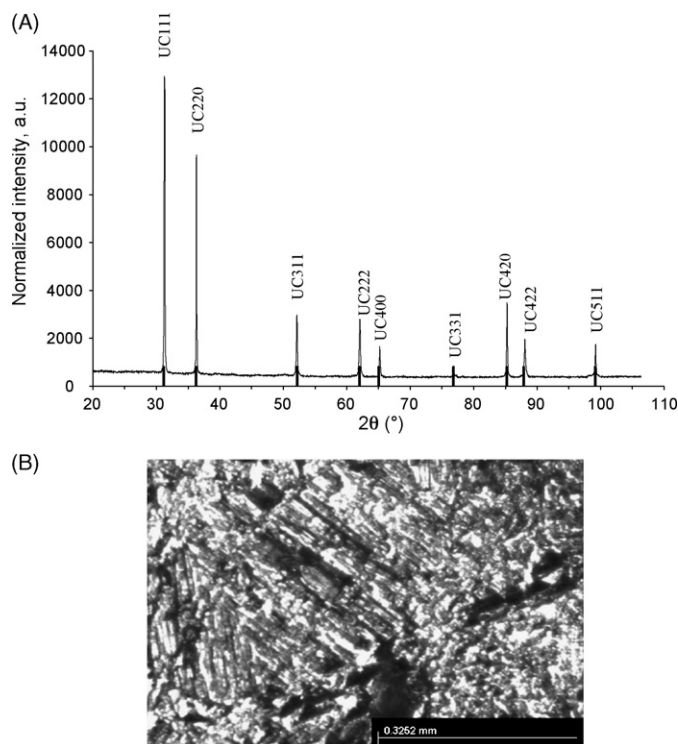


Fig. 1. Characterization of UC ingot used as a working electrode. (A) X-ray diffraction powder pattern. INEL CPS 120 diffractometer, using monochromatized Cu K α 1 radiation. (B) Scanning electron microscopy (SEM) pattern of UC electrode surface.

Prepared ingots were characterized by X-ray diffraction (INEL CPS-120) and scanning electron microscopy (SEM: JEOL-T330A). X-ray powder diffraction analysis (Fig. 1A) confirmed that uranium FCC monocarbide ($4.9608 \pm 0.0005 \text{ \AA}$) [8] was the only phase present in the test ingot. SEM analysis of the electrode surface morphology indicated that the ingot consisted of chaotically oriented and weakly associated 20–50 μm crystallites (Fig. 1B). Energy dispersive spectroscopy (EDS) spectra of the UC electrode indicated that the UC crystallites in air were coated with a thin film of uranium oxycarbide with a C/O ratio of 0.85/0.15 (results not shown).

Prior to each electrochemical measurement, UC electrode surface was treated electrochemically in a 1 M Na_2CO_3 solution (10 cyclic voltammetry scans in the potential interval from -0.1 to 1.5 V/SCE at $dE/dt = 100 \text{ mV s}^{-1}$) under nitrogen atmosphere. Then, the electrode was rinsed with water and stabilized for 20 min in the electrolyte under study to achieve the steady state open circuit potential (OCP) before experimental run. All the experiments were carried out under nitrogen atmosphere. This preliminary treatment allowed to improve the low reproducibility of the electrode surface caused by the chaotic morphology of the samples and by the presence of oxycarbide coating under air atmosphere. However, considering the high surface roughness of the working electrode, it is very difficult to determine the real surface and consequently to estimate the current density at the working electrode.

All solutions were prepared from analytical grade products and pure water (Millipore system). The U concentrations in the solutions were determined by using two methods, time-resolved laser-induced fluorescence spectroscopy (TRLIFS) and capillary electrophoresis (CE), according to the procedures described in [9] and [10].

3. Results

The LV curves recorded at the UC electrode in 0.1–2.0 M HNO_3 (Fig. 2) indicate three ranges of potential corresponding to different processes occurring at the UC electrode in acidic media. In the range from 0 to 400 mV/SCE, the UC electrode

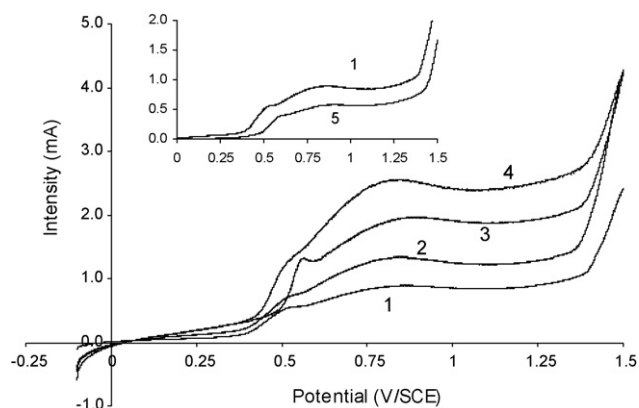
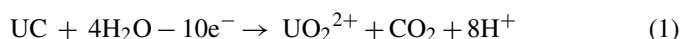


Fig. 2. Linear voltammograms at a static hemispherical UC electrode in acidic solutions, under nitrogen atmosphere at room temperature. $dE/dt = 5 \text{ mV s}^{-1}$. (1) 0.1 M HNO_3 , (2) 0.5 M HNO_3 , (3) 1 M HNO_3 , (4) 2 M HNO_3 and (5) 0.1 M HClO_4 .

was found to undergo slow surface oxidation the most probably accompanied with the formation of a protective layer. The increase of the UC electrochemical oxidation rate was observed at the potentials 450–500 mV/SCE. In the range of potentials from 500 to 1100 mV/SCE a plateau of anodic current, corresponding to moderate rate of UC oxidation was observed. The values of anodic current corresponding to the moderate rate of UC electrochemical oxidation increased with the increase of the electrolyte acidity. The presence of the plateau on LV curves could be associated with simultaneous buildup of the protective layer on the electrode surface and further oxidation with the formation of soluble products. It is important to note that the current peak observed near 0.5 V/SCE, which is characteristic of electrode was generally not reproducible. For example, the three curves plotted in Fig. 2 show very low current peak (for 0.1, 0.5 and 2 M HNO_3) whereas a current peak is visible on the curve for 1 M HNO_3 . The application of the potentials exceeding 1100 mV/SCE to UC surface resulted in the drastic increase of the anodic current, corresponding apparently to the rapid dissolution of the electrode. This increase of the current may be associated with a number of occurring simultaneously anodic reactions including U(IV)/U(VI) oxidation in the surface layer of the electrode and oxidation of the intermediate carbon oxidation product to give CO_2 . The superposition of all occurring electrochemical processes may be described with Eq. (1).



However, the exact value of the number of electrons involved in the resulting anodic reaction would require the careful measurement of the process current efficiency using PCE technique with simultaneous determination of U(VI) and carbon material balance.

Although the nature of the acid anion (NO_3^- or ClO_4^-) and the H^+ concentration in the electrolyte (Fig. 2, inset) did not strongly affect the three potential ranges boundaries, the plateau current corresponding to the moderate UC oxidation rate increased with the acid concentration in the electrolyte from 0.1 to 2 M. This current increase with the increased H^+ concentration in the electrolyte indicated the simultaneous acceleration of

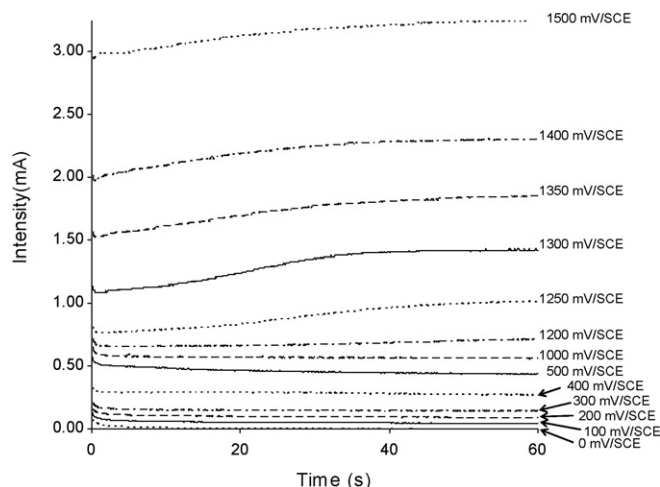


Fig. 3. Multistep potential sweep coulometry (MPSC) at a static hemispherical UC electrode in 1 M HNO₃ solutions, under nitrogen atmosphere at room temperature.

both formation and further oxidation of the protective layer. The diffuse boundary between the slow and moderate UC oxidation rates zones observed in HNO₃ and HClO₄, and the higher current corresponding to the plateau of moderate UC oxidation rates may be accounted for the poor reproducibility of the electrode working surface.

In order to obtain more information about the evolution of UC electrode surface, when the oxidation potential is applied, and thus improve the reproducibility of the experiments, we decided to use another electrochemical technique, the multistep potential sweep coulometry (MPSC) and to observe through this method the electrochemical behavior of UC in HNO₃ and HClO₄ media. This technique was considered to be capable of reproducing the current variation versus the potential by integrating the current at a fixed potential over an extended time period (1 min). Under these conditions, the dissolution of microquantities of UC regenerates the electrode surface condition directly in the test electrolyte.

MPSC measurements were carried out in HNO₃ and HClO₄ (0.1–2 M) in the range of potentials from the open circuit potential –100 to 1500 mV. The current/time (*I/t*) curves at a constant potential *E* obtained in 1 M HNO₃ are shown in Fig. 3.

The character of the current changes in time was different for the three potential ranges pointed out on the LV curves presented in Fig. 2 and was similar in HClO₄ and HNO₃ solutions. In the potential range corresponding to the slow oxidation range, the current evolutions were characterized by a monotonous decrease of the current in time, indicating the increase of the electrode–solution interface resistance. This observation confirms the supposition about the formation of the protection layer at UC surface in this range of potentials. At the boundary between low and moderate oxidation rates, a slight increase of the anodic current was observed after 30–40 s of the current descent. This tends to confirm the contribution of the slow electrochemical reaction resulting in formation of soluble species to the measured value of anodic current. The observed trends in *I* changes with time were characteristic to all the range of poten-

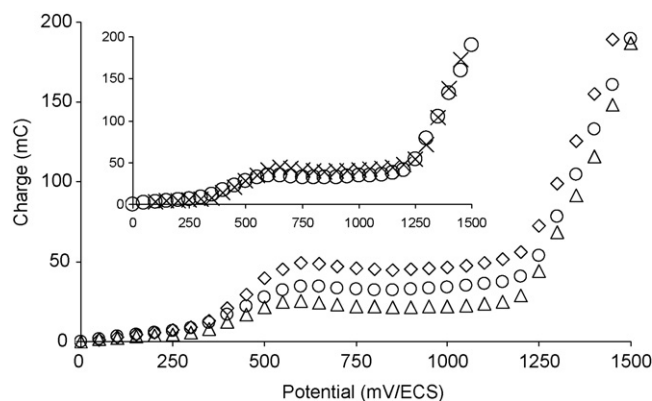


Fig. 4. Charge passed through the cell (integrated current vs. time) as a function of the applied potential (MPSC technique) at a static hemispherical UC electrode in acidic solutions, under nitrogen atmosphere at room temperature. (Δ) 0.5 M HNO₃, (\circ) 1 M HNO₃, (\diamond) 2 M HNO₃ and (\times) 1 M HClO₄.

tial corresponding to moderate UC oxidation rate. The *I*–*t* curves registered at the potentials exceeding 1100 mV/SCE were characterized by a current drop in the first 5–10 s of the run at a given potential, followed by the current increase in time. This increase was more pronounced in the first 20–30 s. The observed current drop could be associated with the fast increase of the surface film resistance after application of the anodic potential pulse, followed by its dissolution at a rate proportional to the applied potential.

The charges (*Q*) obtained by integration of the corresponding *I/t* curves, are summarized for all the range of potential of MPSC measurements in Fig. 4 for both HNO₃ and HClO₄. The results clearly show the presence of three potential zones corresponding to a slow (0–400 mV), moderate (500–1200 mV) and fast (*E* > 1250 mV) UC electrochemical oxidation. The three potential zones did not vary with the test medium (HNO₃ or HClO₄) or with the H⁺ concentration in the electrolyte. Conversely, the plateau current for moderate UC oxidation increased with the H⁺ concentration but did not vary with the medium (HNO₃ or HClO₄). Moreover, the results obtained by using this technique at UC electrode were perfectly reproducible.

The PCE at UC electrode in 1 M HNO₃ was also carried out for 10 min at the potentials 500 mV, 1000 mV and 1300 mV/SCE, corresponding to the boundaries between slow/moderate and moderate/fast UC electrochemical oxidation (Fig. 4). Time duration of the electrolysis was chosen by taking into account the possibility of the mechanical degradation of the electrode surface during electrolysis, resulting in the uncontrolled changes in the electrode specific surface. The kinetic curves of UC anodic dissolution at the chosen potentials are presented in Fig. 5. Presented results showed that, at the potentials below 400 mV/SCE, UC dissolution had been negligible. The increase of the PCE potential resulted in the accumulation of U(VI) in the electrolyte. The increase of U(VI) concentration in time was linear, the dissolution rate increasing with the applied potential. Nevertheless the PCE data confirm the results of *I*–*t* measurements (Fig. 3) and the conclusions on the correspondence between observed current values and UC dissolution rates.

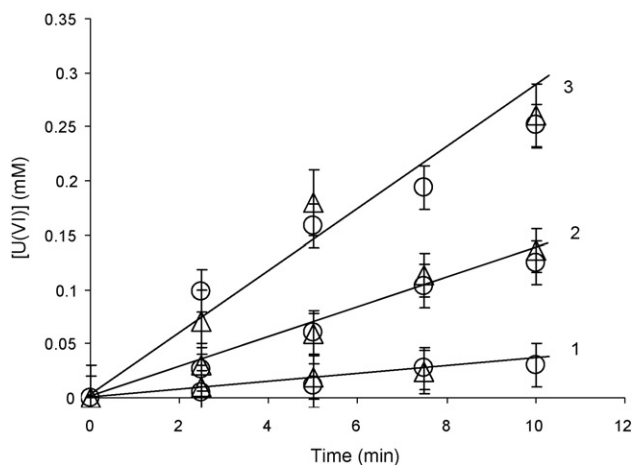


Fig. 5. U(VI) accumulation in 1 M HNO₃ during UC anodic dissolution at different potentials. $T = 22^\circ\text{C}$. 1 – $E = 500\text{ mV/SCE}$, 2 – $E = 1000\text{ mV/SCE}$, 3 – $E = 1300\text{ mV/SCE}$. Measurements carried out by TRLIFS (Δ) and CE (\circ).

4. Discussion

The results of MPSC and LV measurements indicate that the electrochemical behavior of UC was similar in the HNO₃ and HClO₄ (0.1–2 M) solutions. In the range of potentials from the open circuit potential to 0.4 V/SCE, the poorly soluble compound (presumably uranium oxycarbide UC_xO_{1-x}) accumulated at the electrode forms a protective layer. This conclusion is confirmed by the absence of U(VI) in the electrolyte sample taken during MPSC measurement for the electrolysis run performed at $E = 400\text{ mV/SCE}$. It is important to note that, according to the thermodynamic data at the potentials $E < 327\text{ mV/NHE}$ [11], the oxidation state of U in the oxycarbide film recovering the UC electrode does not exceed (+4). The increase of the electrode potential may result in the U(IV)/U(VI) oxidation. Simultaneously, carbon is oxidized with formation of wax resembling compound [12], evidently decreasing the electric conductivity of the electrode. This decrease may in turn increase the U(IV)/U(VI) oxidation overvoltage and prevent from U(VI) dissolution, finally providing the slow electrochemical oxidation of UC.

In the potential interval from 0.4 to 0.6 V/SCE, U(IV)/U(VI) oxidation becomes possible in the oxycarbide film with formation of soluble U(VI), resulting in an increase of the anodic current. However, at these potentials, the UC (or UC_xO_{1-x}) oxidation rate also increases, probably causing an increase in the protective layer thickness and consequently slowing the rate of U(VI) mass transfer through the passive layer. Thus, in the potential range between 0.7 and 1.2 V/SCE, the superposition of the last two processes resulted in steady-state conditions, corresponding to a moderate UC electrochemical oxidation, confirmed by PCE data (Fig. 5).

The anodic current increases rapidly when the UC electrode potential exceeds 1.25 V/SCE. This increase is attributed to

the destruction of the protective film followed by the acceleration of UC dissolution, proved by the appearance of U(VI) in the electrolyte sample taken during MPSC measurement for the electrolysis run performed at $E = 1300\text{ mV/SCE}$. To our opinion, the black, tar resembling film that still exists at the UC the electrode after accomplishing MPSC measurement at 1500 mV/SCE, corresponding to fast UC electrochemical oxidation, consists mainly of polymeric organic species arising from UC carbon oxidation rather than uranium oxycarbide. However, this hypothesis requires careful experimental verification with suitable *in situ* techniques such as coulometry or electrochemical impedance spectroscopy.

5. Concluding remarks

LV and MPSC measurements, for the first time carried out at the UC electrode in 0.1–2 M HNO₃ and HClO₄, show that UC electrochemical oxidation, accompanied by its anodic dissolution, becomes possible at $E > 0.4\text{ V/SCE}$, a value weakly dependent on the electrolyte acidity. In the range of potential between 0.4 and 1.25 V/SCE, UC electrochemical oxidation at moderate rates is observed. In this range of potential, the dissolution is blocked by the formation of a protective film of low solubility composed of the products of primary carbon oxidation. Fast electrochemical dissolution of UC becomes possible at the potentials exceeding 1.25 V/SCE.

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