



Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) modified glassy carbon electrode for electrocatalysis of Pu(IV)/Pu(III) redox couple in 1 M H₂SO₄ medium



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ARTICLE INFO

Article history:

Received 20 October 2016

Received in revised form 5 December 2016

Accepted 13 December 2016

Available online 14 December 2016

Keywords:

PEDOT:PSS/GC

Electrocatalysis

Pu(IV)/Pu(III) couple

detection

DPV

ABSTRACT

Electrocatalytic activity of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) modified glassy carbon electrode is explored for Pu(IV)/Pu(III) redox couple in 1 M H₂SO₄ and its performance is compared with conventionally used electrodes (Au, Pt and GC). The morphology of modified electrode is seen by scanning electron microscopy and its composition is verified by energy dispersive spectroscopy. Cyclic voltammetry and differential pulse voltammetry shows enhanced electrocatalytic activity of modified electrode as it shows maximum current density, least peak potential separation and higher electron transfer rate constant for Pu(IV)/Pu(III) couple as compared to Au, Pt and GC electrode. Electrochemical impedance spectroscopy also confirms our experimental results as the modified electrode shows least charge transfer resistance as compared to conventional electrodes. Trace quantity of Pu detection is possible in a short interval of time with higher sensitivity by differential pulse voltammetry technique that shows the modified electrode can be used for Pu determination in nuclear fuels.

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1. Introduction

Fast Breeder Test Reactor (FBTR) situated at Indira Gandhi Centre for Atomic research (IGCAR), Kalpakkam, India is a breeder reactor used for testing of other fast reactor fuels and materials [1,2]. The reactor uses uranium-plutonium mixed carbide fuel and liquid sodium as coolant. (U_{0.3}Pu_{0.7})C (Mark-I) and (U_{0.45}Pu_{0.55})C (Mark-II) are used as driver fuels in the reactor [2]. Accurate and precise determination of plutonium in the fuels is necessary for safe operation of the reactor. For accurate and precise determination of Pu in nuclear fuel, redox titrimetric methods are generally employed based on end-point detection either by potentiometry or biamperometry techniques [3–5]. The major disadvantage in redox titrimetric method is the addition of chemical reagents during titration, hence, the analytical waste contains metallic impurities (Fe, Ag, Cr, Ti etc.), which makes recovery of Pu from analytical radioactive waste a cumbersome process. Redox titrimetric methods also need chemical standards to ensure the performance of the indicator electrodes and the accuracy of the results.

Although coulometry is an absolute electroanalytical technique which does not require additional chemical reagents and chemical standards [6–10], but it is time consuming. Contrary to that, voltammetry is simple and fast, no chemical additives is required and also gives accurate and precise results. Our group is involved in the development of simple and fast voltammetric techniques for precise and accurate determination of Pu [11–15].

Pt [16], Au [17] and carbonaceous electrodes (glassy carbon [18] and graphite) have been extensively used for studying the electrochemical behaviour of actinides and their determination. However, several disadvantages are associated with these conventional electrodes. Pt and Au electrodes are very often passivated either due to formation of oxides or dissolution of Pt and Au on the electrode surface at higher anodic potentials, normally encountered in non-complexing electrolyte solution of Pu [19,20]. Trace amount of impurities in the electrolyte solution and organic impurities produced during the dissolution of fuel samples, especially Pu carbide fuels, also passivate the surface of Pt and gold electrodes [21]. The electron transfer kinetics at GC electrode is very slow compared to Au and Pt electrodes. Different materials that have been explored in our laboratory to replace these conventional electrodes include metal nanoparticles, conducting polymers, metal-polymer nanocomposites, carbon nanotubes, graphene etc. Pt nanoparticles/GC and Pt nanoparticles/Pt [11],

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Polyaniline/Pt and SWCNT/Pt [12], SWCNT/Au [13], rGO/GC [14], Gr/GC and SWCNT/GC [15] modified electrodes have already been reported to show electrocatalytic activity for Pu(IV)/Pu(III) redox couple and sensitive determination of Pu in acidic solution. Among these, conducting polymers attract a lot of attention due to several advantages like high conductivity, robustness, enhanced performance and low cost. Plutonium electrochemistry on conducting polymer like polyaniline [12] has already been reported, but poly(3,4-ethylenedioxythiophene) (PEDOT) is rarely been explored for actinide electrochemistry. Though, PEDOT is water insoluble, but its composite poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) forms dispersion in water [22]. PEDOT:PSS is a mixture of poly(3,4-ethylenedioxythiophene) and sodium polystyrene sulfonate. PEDOT:PSS is transparent conducting polymer with numerous applications [23–33]. The conductivity of PEDOT:PSS is slightly higher compared to PANI [34] which may result in better electrocatalytic activity of PEDOT:PSS for Pu(IV)/Pu(III) redox couple. In case of PANI/Pt, there is an electrostatic interaction between protonated nitrogen centres in emeraldine salt form of PANI and Pu(IV) anionic complex $[\text{Pu}(\text{SO}_4)_4(\text{H}_2\text{O})_4]^{4-}$, because authors used potassium plutonium sulphate dihydrate ($\text{K}_4\text{Pu}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$) salt dissolved in 1 M H_2SO_4 for studying Pu(IV)/Pu(III) redox couple. There is a possibility pre-concentration of Pu at the surface of PEDOT:PSS/GC, due to the electrostatic interaction between negatively charge PSS and Pu cationic species in 1 M H_2SO_4 and there is possibility of adsorption of Pu(IV) and Pu(III) ions at the electrode surface via interaction with O and S moiety present in the backbone of PEDOT:PSS. Further GC is cheaper

compared to Pt. This motivates us to study the electrochemistry of Pu(IV)/Pu(III) redox couple on PEDOT:PSS modified GC electrodes.

In this paper, to the best of our knowledge, we report for the first time electrochemical studies of Pu(IV)/Pu(III) redox couple in 1 M H_2SO_4 on PEDOT:PSS modified GC electrode and its redox performance is compared with conventionally used electrodes (Pt, Au and GC). The morphology of PEDOT:PSS is seen by SEM and its composition is verified by EDS technique. Its performance towards electrocatalysis of Pu(IV)/Pu(III) couple is assessed by cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS) techniques. Its sensitive response for determination of trace quantity of Pu is examined by oxidation of Pu(III) to Pu(IV) using DPV technique. Its enhanced performance as electrode material for electrocatalysis of Pu(IV)/Pu(III) couple in 1 M H_2SO_4 incites the possible application of commercially available PEDOT:PSS for determination of Pu in nuclear fuels.

2. Experimental section

2.1. Chemicals and apparatus

All the chemical reagents used were of analytical grade and used without any further purification. Solutions used in this study were prepared in deionized water purified by the MilliQ water purifier system from Millipore (18 M Ω cm). Sulphuric acid used in the experiments is of analytical grade. PEDOT:PSS (1.3 wt % dispersion in H_2O) was purchased from Sigma Aldrich. FBTR

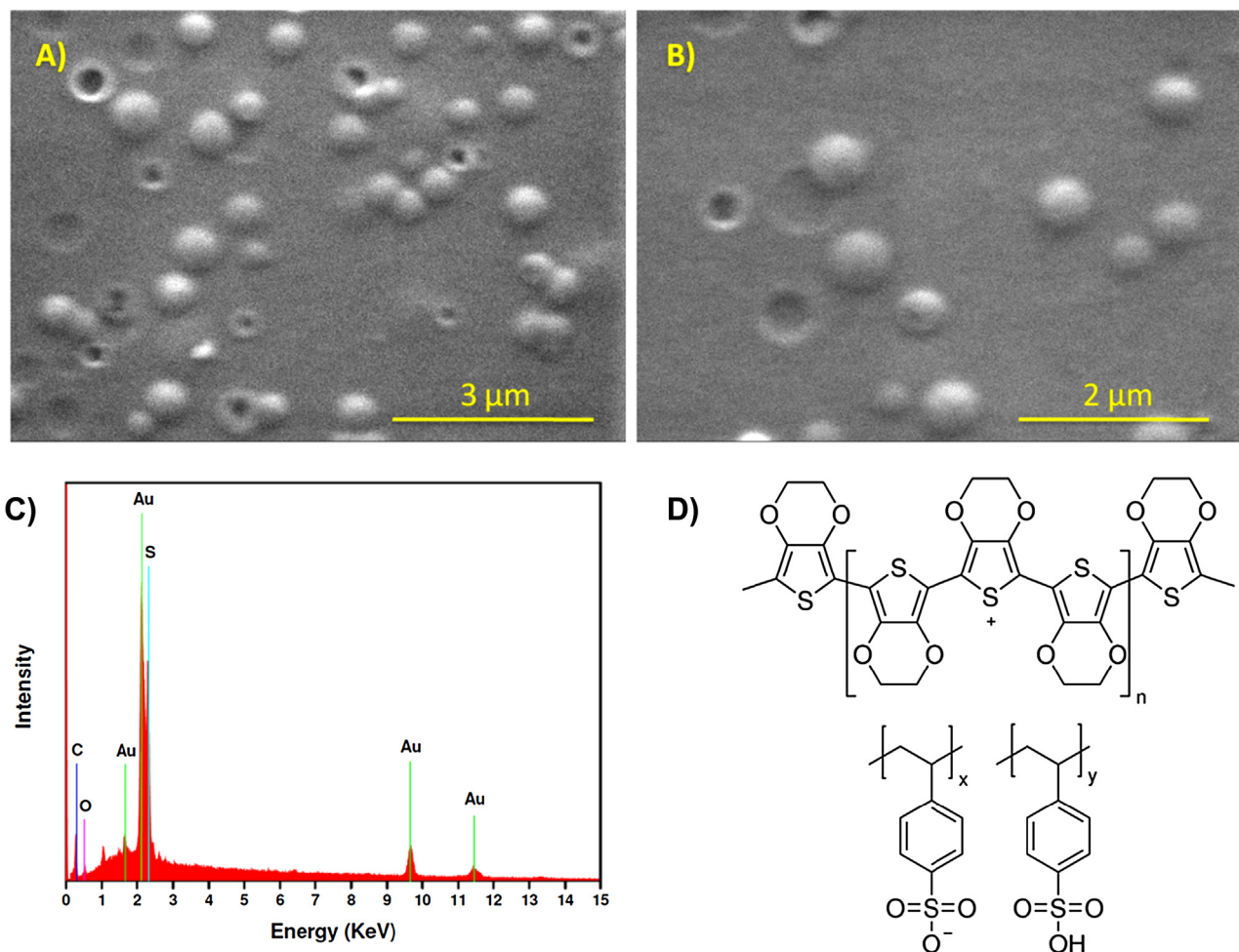


Fig. 1. A–B) SEM images of PEDOT:PSS modified GC; C) EDS spectra of the same and D) chemical structure of PEDOT:PSS.

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