



Characterisation of electrodeposited polycrystalline uranium dioxide thin films on nickel foil for industrial applications



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ABSTRACT

Polycrystalline uranium dioxide thin films were grown on nickel substrates via aqueous electrodeposition of a precursor uranyl salt. The arising semiconducting uranium dioxide thin films exhibited a tower-like morphology, which may be suitable for future application in 3D solar cell applications. The thickness of the homogenous, tower-like films reached 350 nm. Longer deposition times led to the formation of thicker (up to 1.5 μm) and highly porous films.

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1. Introduction

The international nuclear industry is in a state of change. In nuclear-mature countries, there are requirements to shut down, decommission and replace aged nuclear facilities, which have reached the end of their operational lives, along with ongoing requirements to efficiently manage arising and legacy wastes. In other countries, where nuclear energy has little or no history, there are ambitious new-build plans to replace carbon-emitting power plants. According to the World Nuclear Association, each year nuclear power generation facilities worldwide produce about 200,000 m^3 of low- and intermediate-level radioactive wastes, and about 10,000 m^3 of high-level waste, including spent fuel designated as waste. Two different management strategies are used for spent nuclear fuel. In one, the fuel is reprocessed to extract usable material (uranium and plutonium) for new fuel. In the other, spent fuel is simply considered a waste and is stored pending disposal. The main aims of the reprocessing of used fuels are to contribute to energy security by gaining 25–30% more energy from the recovered unused uranium and plutonium in the used fuel elements and reduce the volume of material to be disposed of as high-level waste to about one-fifth.

Electrodeposition can be used as a novel technique for separation of heavy elements from radioactive waste streams [1], for metal target fabrication [2] and/or electronic device applications such as recycled

uranium-based solar cells [3]. There is a need for development of novel techniques for re-use and recycling of nuclear waste rather than disposal. Recent studies reveal a danger of formation of He bubbles affecting the mechanical stability of UO_2 grain boundaries in a closed system, formation of new phase due to oxidation of UO_2 in air or accelerated UO_2 dissolution due to the alpha radiolysis [4]. Thus, the high level of care is required in the case of underground waste storage because of the danger that contamination of the waste with groundwater presents. In addition, radioactive waste disposal is expensive as no facilities or desired infrastructure yet exists worldwide for deep disposal. We propose a cheap method (electrodeposition) of recycling and re-use of nuclear waste. Electrodeposition is the process of using electrodes to apply a current across an electrolytic solution, causing chemical reduction of dissolved metal cations on anodic surfaces to form a coherent coating. In a three electrode cell, cations are deposited on the working electrode composed of a conductive material, such as gold or nickel. A reference electrode is positioned close to a working electrode to assess the relative potential at a point near to the substrate and the counter electrode (usually gold) provides the current to drive the reaction.

Uranium dioxide (UO_2) has previously been electrodeposited onto nickel plates from a uranyl nitrite solution $\text{UO}_2(\text{NO}_3)_2$ in ammonium sulphate [5]. The resulting films were examined with X-ray Photoelectron Spectroscopy (XPS) and confirmed to present a pure UO_2 surface. However, the results were not consistent with supplementary Raman spectra, which indicated the presence of U_3O_8 . Uranium oxides were also previously electrodeposited on nickel substrates from a uranyl

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nitrite solution for target fabrication [6]. However, no detailed characterisation of the arising samples was performed. Uranium dioxide films have also been electrodeposited onto nickel discs using uranyl nitrate in an ammonium oxalate solution under current densities of $40\text{--}150\text{ mA}\cdot\text{cm}^{-2}$, $\text{pH} = 1\text{--}7$ and a temperature of $40\text{--}80\text{ }^\circ\text{C}$ [2]. It has been shown that an electrodeposition current density of $60\text{--}80\text{ mA}\cdot\text{cm}^{-2}$, a temperature of $60\text{ }^\circ\text{C}$, $\text{pH} = 2\text{--}3$ and an electrolyte concentration of $1.67\text{ mg}\cdot\text{mL}^{-1}$ yield uniform uranium oxide thin films, with strong electrode adhesion and a deposition efficiency of $95\text{--}98\%$ [2]. These samples were examined with Energy Dispersive X-ray (EDX) Spectroscopy and Fourier Transform Infrared (FT-IR) Spectroscopy, indicating that uranyl ions were deposited on the cathode in a hydrated polymer form ($\text{UO}_2(\text{H}_2\text{O})_4\text{-O-UO}_2(\text{H}_2\text{O})_4\text{-O}$).

Another application of oxide electrodeposition includes solar cells. Investigation of the development of environmentally-friendly, low cost solar cells with cheaper semiconductor materials is extremely important for the development of viable green energy technologies. Besides as an alternative to conventional semiconductor materials, e.g. Si or GaAs, uranium dioxide is conceptually excellent for niche solar cell applications, e.g. in space. In addition, the use of waste uranium for the manufacture of low cost photovoltaic devices and redox fuel cells [7] may offer an effective way of recycling an otherwise unwanted material, which comes with a long-term storage cost. Table 1 compares the electrical properties of UO_2 and conventional semiconductor materials for solar cell applications.

As seen in Table 1, the band gap of UO_2 lies between those of Si and GaAs, i.e. at the optimum for near maximum solar cell efficiency. The dielectric constant of UO_2 is almost twice that of Si, which also makes UO_2 more suitable for fabrication of higher density integrated circuits with higher breakdown voltages than current Si-based electronics. This also indicates that UO_2 integrated circuits can be much smaller (denser) than conventional integrated circuits. The Seebeck coefficient (a measure of the thermoelectric effect) is also much higher than that for conventional semiconductors, indicating that UO_2 may be an excellent material for incorporation into small thermoelectric energy generators. However, the electronic properties of UO_2 can be dramatically influenced by its stoichiometry. For example, the electrical conductivity of $\text{UO}_{1.994}$ is orders of magnitude lower at higher temperatures than the conductivity of $\text{UO}_{2.001}$. Before uranium-based integrated circuits can be designed and fabricated an appropriate dopant must be selected in order to improve its electronic properties and better control oxide stoichiometry. The doping effect on electrical conductivity of polycrystalline UO_2 samples has been studied in detail using various ion dopants, including Sb, Te, B, P, S and Al [10]. It has been shown that the electrical conductivity strongly depends on dopant concentration. The measured average electrical resistivity of doped samples decreases with the increasing dopant concentration for all elements, excluding B. The most prominent effect is observed for Te and Al dopants. For Al doping, the electric resistivity of a pure UO_2 single crystal decreases from $6.67\text{ }\Omega\text{m}$ down to $5.49\text{ }\Omega\text{m}$ for $10^{17}\text{ Al atoms}\cdot\text{cm}^{-2}$ and to 1.74 for $10^{21}\text{ Al atoms}\cdot\text{cm}^{-2}$. Other UO_2 dopants include oxides such as TiO_2 , Nb_2O_5 , La_2O_3 , Gd_2O_3 and Cr_2O_3 , which produced no significant improvement in the electronic conductivity of UO_2 , and usually exerted a detrimental

effect, excluding Nb_2O_5 , which induced a slight conductivity increase with doping [11].

The objective of the current research was to identify the optimal conditions for electrodeposition of uniform and crystalline UO_2 thin films onto nickel-foil, with the aim of achieving film thickness and structures suitable for novel energy-generating applications such as uranium-based solar cells. Phase and crystalline orientation were measured using X-ray diffraction (XRD). The microstructures of nickel substrates and UO_2 films were determined using scanning electron microscopy (SEM). EDX spectroscopy and secondary ion mass spectrometry (SIMS) were used for mapping and determination of elemental composition. Film thicknesses were measured directly from cross-section analysis using combined focused ion beam (FIB) milling and SEM. Surface morphologies of samples were also studied using high-speed atomic force microscopy (HS-AFM).

2. Experimental methods

2.1. Fabrication

The electrodeposition of uranium oxide was performed at room temperature (RT) in a three-electrode electrochemical cell with a 1 cm^2 nickel foil substrate as the working electrode (WE), a platinum wire as the counter electrode (CE) and a silver/silver chloride (Ag/AgCl) reference electrode (RE). The PGSTAT302N, high current Autolab potentiostat/galvanostat was employed to perform the cyclic voltammetry (CV) and galvanostatic deposition. Before performing the experiment, the nickel foil cathodes were cleaned ultrasonically in ultra-pure isopropanol, acetone, ethanol and distilled water, respectively, for 20 min each.

For all experiments, an electrolyte solution of $0.01\text{ M UO}_2(\text{NO}_3)_2$ containing depleted uranium and $0.5\text{ M }(\text{NH}_4)_2\text{SO}_4$ (the supporting electrolyte) dissolved in 250 ml deionised water was used. The concentration of a starting solution was 0.37% . The pH was adjusted to 3 by adding 0.1 M HNO_3 and the solution was continuously purged with nitrogen gas prior to, and during, the electrodeposition to eliminate any excess oxygen from the system. After deposition, the samples were immediately washed with deionised water and dried with nitrogen gas.

In order to investigate the electrochemical potential of uranium oxide in the acid electrolyte, CV was performed on a pure nickel foil substrate. Fig. 1 shows the cyclic voltammogram of UO_2^{2+} in an electrolyte and in a background solution consisting of $0.5\text{ M }(\text{NH}_4)_2\text{SO}_4$ dissolved in 250 ml deionised water (inset in Fig. 1). In an electrolyte, the potential (E) was changed between -1.1 V and $+1.0\text{ V}$ (vs. Ag/AgCl) and the scan rate was $50\text{ mV}\cdot\text{s}^{-1}$. The voltage minimum observed at -0.77 V

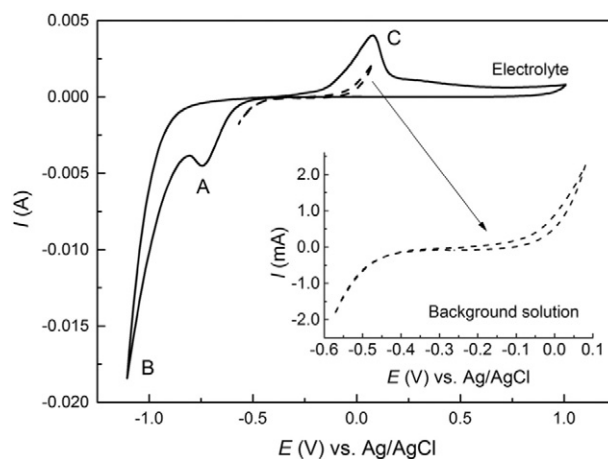


Fig. 1. Cyclic voltammograms of a nickel foil substrate in an electrolytic solution and in a background solution (inset). Points A, B and C label the different stages of UO_2^{2+} deposition (described in the text).

Table 1
Comparison of electrical properties of UO_2 and conventional semiconductors at room temperature [3,8–9].

Properties	Solar cell materials		
	UO_2	Si	GaAs
Band gap (eV)	1.3	1.1	1.4
Dielectric constant	22	11.2	14.1
Seebeck coefficient ($\mu\text{V}\cdot\text{K}^{-1}$)	750	440	100
Thermal conductivity ($\text{W}\cdot\text{m}^{-1}\text{K}^{-1}$)	10	149	52
Electrical conductivity ($\text{S}\cdot\text{m}^{-1}$)	0.15	1.56×10^{-3}	$10^{-8}\text{--}10^3$

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