



# Differential potential pulse deposition of amorphous osmium thin films and electrocatalytic activity for borohydride oxidation in alkaline media

Anna Ignaszak<sup>a</sup>, Előd Gyenge<sup>a,b,\*</sup>

<sup>a</sup> Department of Chemical and Biological Engineering, The University of British Columbia, 2360 East Mall, Vancouver, BC, Canada V6T 1Z3

<sup>b</sup> Clean Energy Research Centre, The University of British Columbia, Vancouver, BC, Canada

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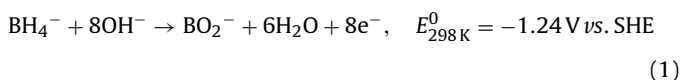
## ABSTRACT

Amorphous Os films (thickness up to 140 nm) were electrodeposited onto Pt/quartz crystal resonator-electrodes by differential potential pulse voltammetry (DPV). The morphological features of the Os films and the associated electrocatalytic activity for  $\text{BH}_4^-$  oxidation in 2 M NaOH were investigated by surface analysis techniques (XPS, SIMS, SEM and XRD) and electrochemical quartz crystal microbalance. The thin films, composed of both metallic Os and  $\text{OsO}_2$ , morphologically are comprised of interconnected agglomerates of 100 nm diameter (or lower). The surface roughness and specific surface area of the Os film can be varied by the number of potential deposition pulses applied, which affects the electrocatalytic activity. These amorphous films demonstrated outstanding electrocatalytic activity for  $\text{BH}_4^-$  oxidation. The Os electrode synthesized with 15 DPV (specific surface area  $3.6 \text{ m}^2 \text{ g}^{-1}$ ) generated a  $\text{BH}_4^-$  oxidation onset potential of  $-0.87 \text{ V vs. SHE}$ , mass activity of  $1240 \text{ A g}^{-1}$  and an electrochemical surface area (ESA) based specific activity of  $347 \text{ A m}^{-2}$ . The mass activity of the amorphous Os thin film was over an order of magnitude higher than previously reported mass activities for carbon-supported polycrystalline Pt or Os catalysts. The high catalytic activity can be partly attributed to the enhanced adsorption of  $\text{BH}_4^-$  on the Os thin film electrode over a wide potential range between  $-0.9 \text{ V}$  and  $-0.2 \text{ V}$ .

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## 1. Introduction

Fuel cells using borohydrides either as hydrogen precursor agent for  $\text{H}_2$ - $\text{O}_2$  cells or as an alkaline solution supplied to the anodes of direct borohydride fuel cells (DBFCs) have received significant attention in recent years [1–5]. One of the challenges for DBFC is the electrocatalysis of  $\text{BH}_4^-$  oxidation, where instead of the complete eight electron process (Eq. (1)), a number of competing partial oxidation pathways generating  $\text{H}_2$  and intermediates of the general form  $\text{BH}_{4-z}(\text{OH})_z^-$  ( $z=1-3$ ) have been proposed on many metals, such as Pt, Au, Pt, Ag, Pd, Ir, Ru, Ni, Rh, etc. or alloys (PtIr, PtRu, PtAu, PtAg, PtNi, PtBi and PdAu) [6–15].



The complex  $\text{BH}_4^-$  oxidation pathways involving faradaic electrocatalytic reactions and/or thermo-catalytic (non-faradaic) hydrolysis can yield overall anywhere between four and eight

electrons per  $\text{BH}_4^-$  anion depending on the electrocatalyst composition, pH, temperature, electrode morphology, electrode potential,  $[\text{BH}_4^-]/[\text{OH}^-]$  concentration ratio and residence time at the electrode surface. In fuel cells where an alkaline  $\text{BH}_4^-$  solution is supplied to the anode, typically the direct eight-electron oxidation would be preferred (Eq. (1)), due to high faradaic efficiency and the absence of *in situ* generated  $\text{H}_2$  gas that could impede the  $\text{BH}_4^-$  mass transfer to the electrode surface and lower the effective ionic conductivity of the alkaline electrolyte. In cases when the evolution of  $\text{H}_2$  gas generated *in situ* by faradaic and/or thermocatalytic hydrolysis pathways cannot be catalytically suppressed [11], the anode should be designed such that to oxidize efficiently the evolved  $\text{H}_2$  in a two-phase (gas/alkaline electrolyte) media. This in fact would constitute an *in situ* alkaline  $\text{H}_2$ - $\text{O}_2$  fuel cell as opposed to what is referred here as DBFC.

Work by Gyenge and co-workers on carbon supported Os nanoparticles synthesized using a modified Bönnerman organosol method, revealed good catalytic activity for direct  $\text{BH}_4^-$  electro-oxidation [16–18]. Moreover, it was estimated that the oxidation process involves seven-electrons on Os nanoparticles, suggesting that reaction pathways leading to  $\text{H}_2$  evolution instead of the preferred  $\text{BO}_2^-$  pathway (Eq. (1)), are hampered [18]. Recently, Lam et al. electrodeposited galvanostatically Os on porous monolithic carbon and graphite-fibre substrates and these electrodes were investigated as anodes in DBFC [19]. This study revealed that the

\* Corresponding author at: Department of Chemical and Biological Engineering, The University of British Columbia, 2360 East Mall, Vancouver, BC, Canada V6T 1Z3. Tel.: +1 6048223217; fax: +1 6048226003.

E-mail address: [egyenge@chbe.ubc.ca](mailto:egyenge@chbe.ubc.ca) (E. Gyenge).

catalytic activity of the electrodeposited Os depends on the nano-structural and crystallographic features of the catalyst, which are influenced, among other variables, by the physico-chemical properties and surface morphology of the carbon and/or graphite-fibre substrates (supports) [19]. In addition to the beneficial short-term electrocatalytic activity determined by half-cell experiments, the stability of the catalytic activity for graphite-fibre supported Os anodes (so called three-dimensional anodes) has been very promising in DBFC experiments [18,19]. These results clearly gave us a strong impetus to further investigate the electrocatalytic activity of Os for  $\text{BH}_4^-$  electro-oxidation.

Density functional theory (DFT) calculations by Escaño et al. predicted that the preferential  $\text{BH}_4^-$  adsorption mode on Os (1 1 1) is undissociative (i.e.,  $\text{BH}_{4,\text{ad}}$ ), as opposed to dissociative adsorption ( $\text{BH}_{4,\text{ad}} \rightarrow \text{BH}_{4-z,\text{ad}} + z\text{H}_{\text{ad}}$ ,  $z = 1-3$ ) on Pt, Ir, Ag, and Pd [11]. The DFT modelling substantiated the role of Os as an effective direct  $\text{BH}_4^-$  oxidation catalyst with minimal  $\text{H}_2$  evolution.

With regards to Os catalyst synthesis, a number of methods have been studied, such as the colloidal organosol method [16,17], chemical vapour deposition (CVD) [20–22], microwave-assisted synthesis [23], template-assisted chemical reduction [24], as well as electrochemical deposition at either constant current [19] or constant potential [25–28]. The hexachloro-osmate ion  $[\text{OsCl}_6]^{2-}$  is a common precursor for Os deposition and it is susceptible to hydrolysis forming  $\text{OsO}_2$ , the pH therefore, is typically controlled between 1 and 1.5 [29a]. The standard potential for  $\text{OsO}_2/\text{Os}$  is 0.69 V vs. SHE [29b].

Depending on synthesis procedure, crystalline [19,20,24] or amorphous [30,31] Os can be obtained. However, there is no in depth information in the literature on the relationship between the Os surface characteristics (determined by the synthesis procedure) and the corresponding catalytic activity for  $\text{BH}_4^-$  electro-oxidation.

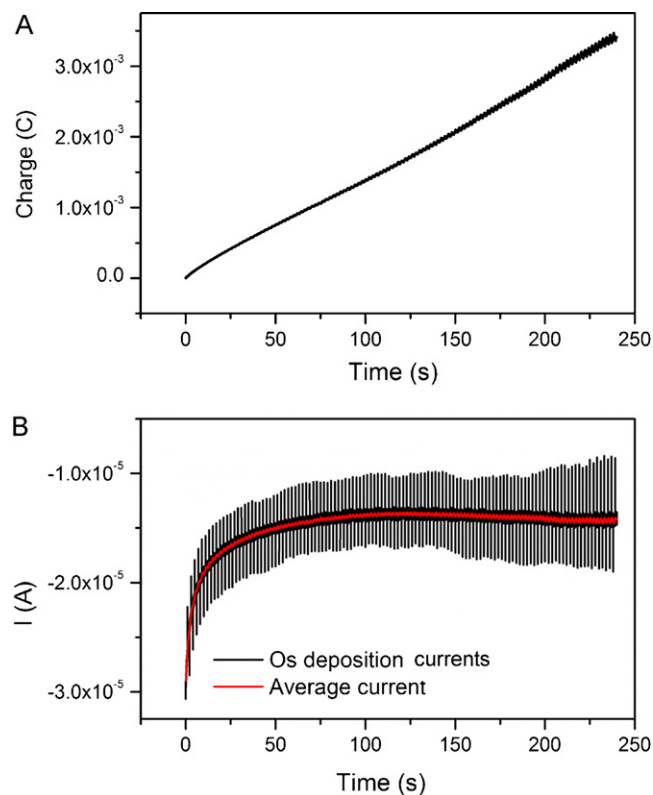
The present work aims to fill this gap, by studying for the first time the properties and electrocatalytic activity of Os thin films electrodeposited by differential pulse voltammetry (DPV). We applied DPV to deposit Os films onto Pt-sputtered quartz crystal resonators. This electrode-resonator assembly setup allowed us to study the electrochemical quartz crystal microbalance (EQCM) behaviour of the deposited Os films in the presence and absence of  $\text{BH}_4^-$ . EQCM has been previously employed by our group to investigate the  $\text{BH}_4^-$  oxidation on Pt and Au electrodes, respectively [10,32].

## 2. Experimental methods

### 2.1. Osmium electrodeposition

Osmium films were electrodeposited by differential pulse voltammetry (DPV) onto AT cut 9 MHz Pt sputtered on quartz crystal resonators (geometric area  $1.96 \times 10^{-5} \text{ m}^2$ , Princeton Applied Research Inc.) using 0.5 mM  $(\text{NH}_4)_2\text{OsCl}_6$  (99.9% Alfa Aesar Inc.) in 0.1 M  $\text{HClO}_4$  (99.999% Sigma–Aldrich Inc.). The water used in all experiments was 18 M $\Omega$  Millipore® Milli-Q®. The three electrode system consisted of the Pt/quartz crystal working electrode, Pt wire counter and Hg/HgSO<sub>4</sub>/0.5 M  $\text{H}_2\text{SO}_4$  (Sentek Ltd.) reference electrodes. The solution was purged with  $\text{N}_2$  (99.995%, Praxair, Canada) for 20 min prior to electrodeposition and during deposition a  $\text{N}_2$  gas blanket at 1 atm(abs) was kept above the solution surface. The Pt resonator-electrode was chemically cleaned by dipping in 0.5 M  $\text{HNO}_3$  for 1 min then rinsing in ultra-pure water, followed by electrochemical cleaning in 0.1 M  $\text{HClO}_4$  with potential scanning between  $-0.2$  and  $1.6$  V at  $0.1 \text{ V s}^{-1}$  (250 cycles).

The differential potential pulse method consisted of step-wise changes of the electrode potential from 0.05 V to 0.03 V vs. SHE with a step height of  $-0.004$  V where each potential step lasted



**Fig. 1.** (A) Average charge passed during 15 DPV deposition pulses; (B) deposition current profile and average deposition current during 15 DPV. 0.5 mM  $(\text{NH}_4)_2\text{OsCl}_6$  in 0.1 M  $\text{HClO}_4$ , 293 K. Substrate: Pt-sputtered quartz crystal.

4 s. Thus, the total time for one pulse was 16 s. This pulse was repeated between five and seventy five times, referred to as 5 and 75 DPV, respectively, allowing the formation of different Os film thickness and surface morphologies. The selected experimental conditions (i.e., deposition potential range and pulsing profile) were determined such that the deposited Os film to cover completely the underlying Pt surface. Fig. 1 shows the average charge and the corresponding deposition current profile for 15 DPV. All the experiments were performed at 293 K.

The electrochemical properties and electrocatalytic activity of the Os films was investigated using the quartz crystal microbalance instrument QCA 922 (Seiko, Princeton Applied Research Inc.) coupled with a PARSTAT 2263 potentiostat (Princeton Applied Research Inc.). The calibration of the Pt/quartz crystal instrument and determination of Sauerbrey constant was performed by anodic stripping of an under-potential deposited Cu layer and it was presented by the present group in an earlier publication [10].

### 2.2. Film characterization

X-ray photoelectron spectroscopy of the deposited Os layers was performed with a Leybold Max 200 spectrometer with a non-monochromatic Mg K $\alpha$  radiation (1253.6 eV) operated at 200 W (10 kV, 20 mA). Prior to individual elemental scans, survey scans were acquired with a 1 eV step to estimate the surface (depth < 10 nm) composition. Narrow scan of Os 4f was obtained with 0.2 eV step size. The XPS spectra have been analyzed using the XPSPEAK 4.1 software utilizing a mixed Gaussian–Lorentzian function (G:L = 85:15) for peak fitting and a Shirley function for the background correction. The peaks were fitted with a full width at half maximum (FWHM) of 1.33 eV. The binding energy of C 1 s (284.5 eV) was used as internal standard.

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