# Solid molybdenum nitride microdisc electrodes: Fabrication, characterisation, and application to the reduction of peroxodisulfate

Saiful Arifin Bin Shafiee, Andrew L. Hector, Guy Denuault*

*Chemistry, University of Southampton, Southampton, SO17 1BJ, UK*

ABSTRACT

A new methodology was developed to fabricate solid molybdenum nitride microdisc electrodes for the first time. The MoN microrods were produced by heating Mo microwires in dry $NH_3$ atmosphere for several hours. They were characterised by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD). The latter revealed the samples had crystallised in the $\delta_3$-MoN phase with a core of $\gamma$-$Mo_2N$. Their electrochemical behaviour was probed for the reduction of $Ru(NH_3)_6^{3+}$. For this fast electron transfer the MoN microdisc electrodes returned similar voltammetric features to Pt microelectrodes. Their amperometric response was further tested with the reduction of peroxodisulfate. In contrast with other electrode materials, the reduction of $S_2O_8^{2-}$ on MoN microdiscs delivered steady state voltammograms with well-defined diffusion controlled plateau. At low sweep rates, the limiting current was consistent with hemispherical diffusion and stable for at least 500 s. The diffusion coefficient of $S_2O_8^{2-}$ derived from these results, $9.5 \times 10^{-6}$ $cm^2\,s^{-1}$, is in excellent agreement with previous work. At high sweep rates, the reduction of peroxodisulfate was found to be complicated by the simultaneous reduction of adsorbates. The results indicate that MoN is an ideal electrode material to monitor the concentration of peroxodisulfate under steady state conditions.

© 2018 Published by Elsevier Ltd.

## 1. Introduction

The electrochemical behaviour of metal nitrides, MoN included, has not been widely studied. Amorphous films of CoN have been found to have good properties for the oxygen reduction reaction (ORR) but are unfortunately unstable near the ORR onset potential [1,2]. MoN materials are typically prepared as thin films [3,4] with thicknesses ranging from 0.5 to 20 μm and are usually made via physical vapour deposition [5,6] or chemical vapour deposition [7,8]. Thin film MoN electrodes have been examined by a few groups [8—11] but in most cases the electrodes were used as capacitors or as electrocatalysts for the oxygen reduction reaction (ORR) [7,9,12]. During fabrication and use these films often crack and delaminate [13] thereby producing higher surface areas and exposing the underlying substrate. In this paper, we demonstrate the viability of producing solid MoN microelectrodes which do not suffer these limitations. In brief, we prepare MoN microelectrodes from Mo microwires via ammonolysis and after characterisation we

exploit them for electroanalytical purposes. In particular we investigate the electroreduction of peroxodisulfate ($S_2O_8^{2-}$) which has complicated voltammetry on common electrode materials [14,15]. We show that on MoN microdiscs the reduction of $S_2O_8^{2-}$ can be diffusion-controlled without having to modify the electrode surface.

Molybdenum nitride exists in many structural forms. $\alpha$-$MoN_x$ is Mo metal with small amounts of interstitial N [16]. $\gamma$-$Mo_2N$ adopts the cubic rocksalt structure with around 50% vacancies on the anion sites, and $\beta$-MoN is a tetragonal distortion of the $\gamma$-$Mo_2N$ with N atoms displacements [16,17]. Different phase constituents can be obtained by controlling parameters including the temperature during the synthesis [3]. For example, $\beta$-MoN is stable at low temperature and $\gamma$-MoN is stable at high temperature [17]. There are several types of hexagonal ($\delta$-) MoN [17]. $\delta_1$-MoN consists of a WC-type crystal lattice with stacking faults of the N atoms layers along the *c*-axis. $\delta_2$-MoN has a NiAs type structure and $\delta_3$-MoN can be described as a slightly distorted NiAs superstructure. $Mo_5N_6$ is the outcome of coalescence of WC- and NiAs-type building blocks with vacancies on Mo sites. In this work, several characterisations were performed on the MoN samples before recording their electrochemical response. Little is known about their electrochemistry

but Cao et al. reported that δ-MoN is a better ORR catalyst than the γ-Mo$_2$N phase [12].
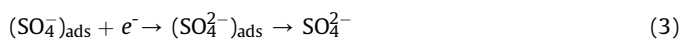
Peroxodisulfate, also known as peroxydisulfate and persulfate, is a strong oxidising agent which has been used to decompose organic compounds [18], particularly in wastewaters. According to Botukhova and Petrii, the peculiar voltammetry of S$_2$O$_8^{2-}$ was first reported in 1949 [15]. Many electrode materials have been employed over the years, either pristine or modified surfaces, to further understand the electrochemical behaviour of S$_2$O$_8^{2-}$. Some of the materials include polycrystalline Au [14], single crystals of Au [19,20], roughened Au [21], Pt [15], bismuth modified Pt [15,22], cadmium and lead modified Pt [23], thallium modified Pt [24], Prussian blue modified Pt [25], modified carbon nanotubes [26], and boron-doped diamond [27]. Most of the studies were conducted using rotating disc electrodes (RDE). In this work, we have employed microelectrodes which are known to have high mass transfer coefficient, low ohmic drop, and low double layer charging current [28].

Although the diffusion-controlled reduction of S$_2$O$_8^{2-}$ has been reported, in most cases the RDE voltammograms are poorly-defined and only reach a limiting current in a narrow potential window. To the best of our knowledge, the only materials that demonstrate sigmoidal shape RDE voltammograms are the bismuth and lead-modified Pt electrodes [15,22,23]. In all cases the stability of the amperometric response is not mentioned.

Overall the reduction of S$_2$O$_8^{2-}$ is a two-electron process [21]:

$$S_2O_8^{2-} + 2\ e^- \rightarrow 2\ SO_4^{2-} \tag{1}$$

However the reaction mechanisms proposed to explain its voltammetry are complex and generally involve dissociative chemisorption of an intermediate. For example the mechanism proposed by Samec and co-workers for the reduction of S$_2$O$_8^{2-}$ on gold involves two pathways [14]. The first occurs at more positive potentials and involves the fast dissociative chemisorption of intermediates followed by their reduction in a slow one-electron process:

$$S_2O_8^{2-} \rightarrow (S_2O_8^{2-})_{ads} \rightarrow 2(SO_4^-)_{ads} \tag{2}$$

$$(SO_4^-)_{ads} + e^- \rightarrow (SO_4^{2-})_{ads} \rightarrow SO_4^{2-} \tag{3}$$

while the second occurs at more negative potentials and involves two consecutive one-electron transfers:

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + SO_4^- \tag{4}$$

$$SO_4^- + e^- \rightarrow SO_4^{2-} \tag{5}$$

Whatever the electrode material, it is clear that the adsorption process complicates the mechanism and it is of interest to find a material that can promote the mass transport controlled reduction of peroxodisulfate.

We first report the fabrication and characterisation of the MoN microdisc electrodes then present their electrochemical behaviour with a model redox compound before discussing the electrochemistry of peroxodisulfate.

## 2. Experimental

A 25 μm diameter Mo wire (99.95%, Advent Research Materials) was cut into several 5 mm long pieces. The wires were then laid in between two alumina tiles to prevent them from bending or curling during the ammonolysis. The tiles were placed in the middle of a silica tube located inside a programmable tube furnace (Lenton Thermal Designs Limited). Dry ammonia gas (BOC anhydrous grade, further dried with molecular sieves) was flowed through the sample tube during the entire nitridation process. The temperature was raised (10 °C min$^{-1}$) to 800 °C, held at this value for 60 h, raised (10 °C min$^{-1}$) to 1100 °C, held at this value for 30 h, decreased (10 °C min$^{-1}$) to 800 °C and held at this value for a further 15 h. The sample was left to cool to room temperature under ammonia then flushed with nitrogen for 15 min to remove excess ammonia. The SEM images and the EDS spectra of the samples were acquired using a Phillips XL 30 ESEM with a Thermofisher Ultradry detector. The XRD analysis was performed using a Rigaku SmartLab diffractometer with Cu-K$_\alpha$ radiation and a DTex-250 1D detector. XRD patterns were collected in transmission mode with a 0.2 mm line beam and the samples glued to a Scotch Magic tape (3M), or with a 0.1 mm spot on a polished microelectrode cross-section. The XRD data was analysed and treated using the PDXL2 software. Rietveld refinement was carried out using the GSAS package [29] with model structures from the Inorganic Crystal Structure Database [30].

To fabricate the MoN microdisc electrodes, one end of the MoN wire was connected to a copper wire (RS Components) using silver epoxy (RS Components). A 1 mL pipette tip (Diamond) was bisected and covered with Teflon tape then used as a mould for the electrode fabrication. A small amount of epoxy resin (Araldite) was deposited inside the mould. The wire was laid on top of the epoxy resin before adding more epoxy resin to completely cover the wire. The epoxy was allowed to harden overnight thus providing a solid insulating sheath to the otherwise brittle MoN wires. The hardened epoxy was polished with silicon carbide papers (Starke) of different grades (200, 600, and 1200) to expose the MoN microdisc. The electrode was then polished with alumina lapping films (3M) of different grades (5, 1 and, 0.3 μm) to obtain a mirror finished surface. The electrode surface was cleaned using a wetted microcloth (Buehler) and deionised water.

All chemicals were used as received without further purification. The K$_2$S$_2$O$_8$ (≥99%) and KCl (≥99%) were obtained from Fluka and Fisher Scientific respectively. The Ru(NH$_3$)$_6$Cl$_3$ (98%) and KClO$_4$ (≥99.99%) were both obtained from Aldrich. The deionised water (resistivity 18.2 MΩ cm) was acquired from a Purite Select water purification system to prepare the aqueous solutions and to clean the glassware. The glassware was soaked in Decon 90 (BDH) overnight. It was then rinsed with copious amounts of deionised water before being dried in an oven (LTE Scientific) at 40−50 °C before use. Five-neck cells were used to hold the test solutions. The electrochemical experiments were conducted inside a grounded Faraday cage to reduce the electromagnetic noise and performed using an Autolab PGSTAT101 controlled with NOVA 1.10, both from EcoChemie. The experiments were conducted at room temperature (19−23 °C). The test solutions were thoroughly deoxygenated with Ar gas (BOC) for 30 min, then for 15 min before recording the voltammetric responses. To maintain reproducibility, the electrode was polished for 10 min with 0.3 μm alumina lapping film to expose a pristine MoN surface before each experiment.

## 3. Results and discussion

### 3.1. Material characterisation

XRD was performed on the MoN samples to determine the phase produced during ammonolysis. Fig. 1 shows a Rietveld fit to a typical diffraction pattern obtained with the MoN wires in transmission mode. The broad background arises from the Scotch tape used to mount the fragile wires in the beam (see Fig. SI1 for a spectrum of the background). The δ$_3$-MoN phase (lattice parameters $a = 0.574(3)$ and $c = 0.563(3)$ nm) accounts for most of the