Redox, surface and electrocatalytic properties of layer-by-layer films based upon Fe(III)-substituted crown polyoxometalate [P8W48O184Fe16(OH)(28)(H2O)(4)](20-)

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N.B.: When citing this work, cite the original article.

Original Publication:
http://dx.doi.org/10.1016/j.electacta.2014.03.099
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http://www.elsevier.com/

Postprint available at: Linköping University Electronic Press
http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-109221
Redox, surface and electrocatalytic properties of layer-by-layer films based upon Fe(III)-substituted crown polyoxometalate

$[P_8W_{48}O_{184}Fe_{16}(OH)_{28}(H_2O)_4]^{20-}$

Rashda Naseer, a Sib Sankar Mal, b Masooma Ibrahim, b Ulrich Kortz, b Gordon Armstrong, c Fathima Laffir, c Calum Dickinson, c Mikhail Vagin, d* Timothy McCormac a

aElectrochemistry Research Group, Department of Applied Science, Dundalk Institute of Technology, Dublin Road, Dundalk, County Louth, Ireland
Tel: +353 42 937 4579; Fax: +353 42 933 1163; e-mail: tim.mccormac@dkit.ie

bSchool of Engineering and Science, Jacobs University, P.O. Box 750561, 28725 Bremen, Germany
Fax: (+49) 421-200-3229; e-mail: u.kortz@jacobs-university.de

cMaterials and Surface Science Institute, University of Limerick, Limerick, Ireland
Tel: +353 61 213127, Fax: +353 61 213529

dDepartment of Physics, Chemistry and Biology, Linköping University, SE-581 83, Linköping, Sweden; Tel: +46702753087; e-mail: mikva@ifm.liu.se

Abstract

The electrocatalytic ability of the iron-substituted crown-type polyoxometalate (POM) $Li_4K_{16}[P_8W_{48}O_{184}Fe_{16}(OH)_{28}(H_2O)_4]^{66H_2O·2KCl}$ (P$_8$W$_{48}$Fe$_{16}$) towards the reduction of both nitrite and hydrogen peroxide reduction has been studied in both the solution and immobilized states for the POM. P$_8$W$_{48}$Fe$_{16}$ was surface immobilised onto carbon electrode surfaces through employment of the layer-by-layer technique (LBL) using pentaerythritol-based Ru(II)-metalloendrimer [RuD](PF$_6$)$_8$ as the cationic layer within the resulting films. The constructed multilayer films have been extensively studied by various electrochemical techniques and surface based techniques. Cyclic voltammetry and impedance spectroscopy have been utilized to monitor the construction of the LBL film after the deposition of each monolayer. The electrochemical behaviour of both a cationic and anionic

* Corresponding author
redox probes at the LBL films has been undertaken to give indications as to the film’s porosity. The elemental composition and the surface morphology of the LBL films was confirmed through the employment of AFM, XPS and SEM.

**Keywords:** polyoxometalate, electrocatalysis, layer-by-layer, iron-substituted crown-type POM, nitrite reduction, peroxide reduction
1. Introduction
Polyoxometalates (POMs) are a large family of inorganic metal oxide cluster compounds which possess multiple redox transfers primarily associated with the ability of their metal-oxide frameworks to accept multiple electrons reversibly. It is this property which has seen POMs being utilised across a wide domain of applications [1-6]. A large majority of these applications require effective surface immobilisation of the POM moiety, various strategies have been employed to this end, including, conducting polymers, Langmuir-Blodgett and sol-gel films, the layer-by-layer (LBL) technique, passive diffusion, electrodeposition and self-assembly [7-15]. The LBL technique, which is rapid and simple, is based upon the electrostatic attractions between oppositely charged moieties [16-19]. It results in highly uniform and stable films that possess a high degree of structural and functional control and can be applied to substrates like carbon, glass, silicon and quartz [16, 20].

A variety of charged moieties have been employed for the construction of LBL assemblies, including polycations, such as, poly(diallyldimethylammonium chloride) (PDDA), poly(ethyleimine) (PEI) and poly(allylaminehydrochloride) (PAH) [21-29], transition metal complexes [16], dye molecules such as Methylene Blue, Thionin, Azure A, Brilliant Cresyl Blue and Nile Blue chloride [30], metallodendrimers [31], dendrimers [18], metalloporphyrins [32] and nanoparticles [33]. The growth of such films on solid surfaces has been monitored by cyclic voltammetry [16, 20, 22, 31, 34-36], UV - Vis absorption spectroscopy [16, 20, 22, 30, 35, 36] or impedance spectroscopy [20]. The LBL films have then been characterised by electrochemical quartz crystal microgravimetric technique [16], SEM [36, 37], AFM [22, 30, 31, 38], XPS [22, 31, 38], fluorescence spectroscopy [37], FTIR spectroscopy [30] and electron spin resonance techniques (ESR) [22].

The regularity of molecular structures of dendrimers offers the route towards well-defined surface functionality, which results in advanced properties in comparison with polymers [39, 40]. Metal ion-substituted dendrimers showed an enhancement of catalytic properties [41] and offered the sites for electron transfer mediation [42]. Ruthenium metallodendrimer became an excellent cationic moiety for the
immobilization of POMs via LBL assembly [43-45] combining the anodic mediation function [35] and the charge matching with that of the POM contributing the film stability [31].

In this contribution the crown-type polyoxometalate Li₄K₁₆[P₈W₄₈O₁₈₄Fe₁₆(OH)₂₈(H₂O)₄]-66H₂O·2KCl (P₈W₄₈Fe₁₆) has been employed as an electrocatalyst for both nitrite and hydrogen peroxide reduction. Two competitive experimental approaches were used for the comparison of analytical characteristics: solution of electrocatalyst and its immobilization onto electrode surface due to LBL assembly with cationic ruthenium metallodendrimer. Electrochemical methods as well as physical methods of surface analysis have been employed for the characterization of LBL film-modified electrode. The electrochemical activity of electrocatalyst in solution showed higher sensitivity in comparison with characteristics of catalyst-based in LBL film used for the catalyst immobilization onto electrode surface.

2. Experimental

2.1 Materials

The crown-type POM Li₄K₁₆[P₈W₄₈O₁₈₄Fe₁₆(OH)₂₈(H₂O)₄]-66H₂O·2KCl, termed P₈W₄₈Fe₁₆ herein after (Fig. 1A) has been synthesised and characterised according to the literature [46]. The pentaerythritol-based Ru-metalloendrimer [RuD](PF₆)₈ (termed herein after as RuD (Fig. 1B)) was synthesized following the method reported by Constable [47] and Holmstrom [42]. At the first stage, four terpyridine metal-binding units were attached to the pentaerythritol by the reaction with 4'-chloro-terpyridine in presence of potassium hydroxide in DMSO. At the second stage, RuD was precipitated as hexafluorophosphate salt from the water-dissolved red product of the reaction of ruthenium(III)-terpyridine chloride with terpyridin-modified pentaerythritol in in ethane-1,2-diol in the presence of N-ethylmorpholine and purified with chromatography.

Poly(diallyldimethylammonium chloride) (PDDA, MW 20,000) and all other chemicals were purchased from Aldrich and were used without further treatment. HPLC grade water was used for the preparation of all aqueous solutions. The aqueous
buffer solutions were prepared from 0.5M Li$_2$SO$_4$ + 0.5M H$_2$SO$_4$ (pH 2.0), 0.5M H$_2$SO$_4$ (pH 0.0 - 0.5), 1M LiCl + 1M HCl (pH 1.0 - 3.0), and 1M CH$_3$COOLi + 1M CH$_3$COOH (pH 3.5 - 7.0). For the electrocatalysis experiments solutions of NaNO$_2$ and H$_2$O$_2$ were freshly prepared before use.

2.2. Apparatus and procedures
2.2.1 Electrochemical measurements
All electrochemical experiments were performed with a CHI660 electrochemical work station employing a conventional three-electrode electrochemical cell. A glassy carbon electrode (GCE, 3 mm diameter, surface area 0.0707 cm$^2$) was used as the working electrode, a platinum wire as the auxiliary electrode, and a silver/silver chloride as the reference electrode (3M KCl) in aqueous media in all experiments unless otherwise stated. Prior to use the working electrode was successively polished with 1.0, 0.3 and 0.05 µm alumina powders and sonicated in water for 10 min after each polishing step. Finally, the electrode was washed with ethanol and then dried with a high purity argon stream. All solutions were degassed for at least 20 min with high-purity argon and kept under a blanket of argon during all electrochemical experiments.

2.2.2 Construction of multilayer assemblies
A freshly polished glassy carbon electrode (GCE) was immersed in the 8% (v/v) PDDA solution for one hour for initial surface modification. Then electrode was then rinsed thoroughly with deionised water and dipped in a 0.25mM solution of P$_8$W$_{48}$Fe$_{16}$ in pH 2 buffer solution for 20 minutes to allow the initial anionic layer to adsorb (Step 1). The modified electrode was rinsed again thoroughly with deionised water and dried with a high purity nitrogen stream. This yielded the PDDA/P$_8$W$_{48}$Fe$_{16}$ modified electrode which was then dipped in a 0.2 mM solution of RuD in acetonitrile for 20 minutes (Step 2). The electrode was then washed with acetonitrile and dried with nitrogen. To build the desired number of layers, steps 1 and 2 the ‘POM’ were repeated in a cyclic fashion. The outer layer of the multilayer assembly was chosen so as to be either anionic or cationic in nature.

2.2.3 Electrochemical Impedance Spectroscopy (EIS)
Electrochemical impedance spectroscopy has been carried out in a 10 mM potassium ferricyanide and 10 mM potassium ferrocyanide solution in 0.1 M KCl at an applied potential of +230 mV (versus Ag/AgCl) from 0.1 to $10^6$ Hz with a voltage amplitude of 5 mV.

2.2.4 X-ray photoelectron spectroscopy

LBL films deposited on ITO slides were characterized using XPS. Analysis was performed in a Kratos AXIS 165 spectrometer using monochromatic Al Kα radiation of energy 1486.6 eV. Survey spectra and high resolution spectra were acquired at fixed pass energies of 160eV and 20eV, respectively. In the near-surface region the atomic concentrations of the chemical elements were evaluated after subtraction of a Shirley type background by considering the corresponding Scofield atomic sensitivity factors. Surface charge was efficiently neutralized by flooding the sample surface with low energy electrons. Core level binding energies were determined using the C 1s peak at 284.8 eV as the charge reference.

2.2.5 Scanning Electron Microscopy

SEM imaging was carried out on a Hitachi SU-70 field emission scanning electron microscope operating at an accelerating voltage of 3 kV. The low voltage allowed for imaging the POM without the requirement of a gold coating. Energy dispersive spectroscopy was collected using the Oxford Instruments X-Stream EDS detector operating at an accelerating voltage of 20 kV and analyzed using their INCA software. Due to the high penetration depth for this voltage resulting in strong peaks coming from the substrate, all spectra were plotted on a Log scale in order to view the peaks from the POM.

2.2.6 Atomic force microscopy

The LBL films formed on ITO slides were imaged in air using an Agilent 5500 operating in AAC (‘tapping’) mode, controlled by PicoView 1.10 software. Micromasch NSC14 cantilevers (160 kHz typical resonant frequency, 5 N/m spring constant) were used. All images presented were obtained at 256 pixel resolution. Scan areas and scan speeds were optimized to suit the features observed for each sample; typically, scans of 1 x 1 μm were obtained at a scan speed of 0.7 lines/second.
Images were processed using PicoImage Advanced 5.1.1 software. Raw topography and amplitude data images were levelled using a three-point algorithm. Where appropriate, noise was removed by applying a median denoising spatial filter and line noise arising from artefacts was removed. The resulting topography images are presented as pseudo-colour images. Height parameters were determined for each topography image according to ISO standard 25178.

### 3 Results and Discussions

Electrochemical properties of the $P_8W_{48}Fe_{16}-RuD$-based LBL films and their inherent electrocatalytic activities towards nitrite and hydrogen peroxide reduction have been studied and compared with the solution behaviour of the $P_8W_{48}Fe_{16}$ and its iron-free precursor. The employment of RuD as a counter-partner for LBL assembly with $P_8W_{48}Fe_{16}$ is due to good balance of charge leading to films of high stability [31]. The LBL assembly has been monitored by voltammetry and EIS. Redox probes have been utilised for the assessment of the film’s porosity and associated electrode kinetics. The constructed layers were then characterised through the employment of electrochemical and surface based techniques (AFM, SEM and XPS).

#### 3.1 Solution electrochemistry

Figure 2A represents the cyclic voltammogram obtained at the bare GCE in pH2 for the Fe$^{3+}$-substituted POM, $P_8W_{48}Fe_{16}$ and its precursor [P$_8$W$_{48}$O$_{184}$]$^{40-}$. The cathodic and anodic peaks at -0.22V and +0.59V in the voltammogram for the $P_8W_{48}Fe_{16}$ represent the simultaneous one-electron reduction and corresponding reoxidation of the POM’s 16 Fe(III) centres [46]. The absence of these iron based redox processes is evident in the cyclic voltammogram for the precursor [P$_8$W$_{48}$O$_{184}$]$^{40-}$. The redox processes, labelled I and II, which are observed at $E_{1/2}$ values of -0.33 and -0.54V respectively, represent the two consecutive eight-electronic redox-processes of the POM’s tungsten-oxo (W-O) framework. These results are in good agreement with the literature [46].

Figure 2B illustrates the voltammetric responses of $P_8W_{48}Fe_{16}$ both in the absence and presence of various concentrations of NaNO$_2$. An increase in the cathodic
current associated with the W-O II redox process is observed with an associated reduction in the redox process’s anodic counterpart upon the addition of NaNO₂. The resulting calibration plot (Inset of Fig. 2B) shows linearity in the concentration range between 0.2 mM to 4.0 mM of nitrite with a measured sensitivity of 0.025 A/(M·cm²), with the latter being calculated from the low concentration domain of the calibration plot. Due to the inherent instability of HNO₂ (pKₐ 3.3) via a disproportionation reaction [48] the electrocatalytic response of the POM in solution towards the reduction of nitrite has been studied at pH 4.5 (data not shown). Interestingly it appears that the current associated with the POM’s first W-O redox process is significantly enhanced upon the addition of nitrite. The resulting calibration plot at pH 4.5 shows the same linearity range as found at pH 2. However the sensitivity, calculated from the low concentration domain of the calibration plot, was 0.08 A/(M·cm²), which is higher than that found at pH 2. In addition, there is no electrocatalytic response between the POM and nitrate up to 10 mM concentration (data not show). Therefore it can be concluded that the P₈W₄₈Fe₁₆ showed excellent selectivity towards the reduction of nitrite as shown with polyoxometalates in general [49-52]. The electrocatalytic current increase has been observed with the W-O II redox process of the precursor K₂₀Li₅[H₇P₈W₄₈O₁₈₁]·92H₂O (data not shown). However, the catalytic current increase was smaller for the precursor POM than for P₈W₄₈Fe₁₆. Thus the insertion of Fe³⁺-ions plays a significant role in the electrocatalytic reduction of the added nitrite.

The ability of the P₈W₄₈Fe₁₆ POM towards the electrocatalytic reduction of hydrogen peroxide has also been investigated (Fig. 2C). There appears to be enhancement of the current associated with the 2nd W-O redox process upon the addition of hydrogen peroxide. The concentration dependence of the resulting catalytic currents measured at the W-O II potential (i.e. -0.55 V) showed linearity in the concentration range between 0.2 mM to 11 mM for hydrogen peroxide. The measured sensitivity towards hydrogen peroxide was found to be 0.026 A/(M·cm²).

3.2 P₈W₄₈Fe₁₆ LBL films
3.2.1 Redox Behaviour

Cyclic voltammetry was utilised to monitor the growth of the LBL assemblies after the deposition of each anionic POM (Fig. 3A) and cationic RuD layer (Fig. 3B). It can be seen from these figures that the redox processes associated with both the P$_8$W$_{48}$Fe$_{16}$ and the RuD moieties within the films are observed. With the addition of each layer there is a gradual increase in the peak currents for the observed redox processes, this being more prominent for the POM’s W-O (II) and Fe(III/II) oxidation processes, and for the RuD’s Ru(III/II) redox process. Whereas the peak currents associated with the POM’s W-O (I) redox process do not increase markedly with layer number and the reduction peak associated with the reduction of the POM’s Fe(III) centres is only observed upon the deposition of the initial POM layer. Comparison of the peak currents associated with the Ru(II/III) redox process in Figures 3A and 3B reveals that this redox process is partly suppressed by deposition of each RuD layer: up to two times a decrease for the oxidation peak and up to five times a decrease for the reduction peak at 20 layers.

Figure 3C represents the dependence of the charges associated with the W-O II and RuII/III redox processes upon layer number. It has been observed, that the nature of the film’s outer layer has a significant effect upon the the RuII/III redox process but less so on the W-O II redox process. The possible reason is that different outer layers, whether they are cationic or anionic in nature, might have different densities and permeabilities towards counter ions which must pass into the film from the supporting electrolyte for reasons of charge neutrality during the redox processes. The behaviour shown in Figure 3C appears to be inherent to P$_8$W$_{48}$Fe$_{16}$-based LBL films as it has been observed previously for such films [53]. The surface coverage of the films was calculated employing $\Gamma = \frac{Q}{nFA}$, where Q is the peak charge (C) associated with a particular redox process of the film, n the number of transferred electrons for this redox process, which is equal to 8 for the W-O redox processes of the crown type heteropolyanions P$_8$W$_{48}$Fe$_{16}$ [54], F is Faraday’s constant (96,485 C mol$^{-1}$) and A is the electrode surface area (0.0707 cm$^2$). The values for the film’s surface coverage as a function of layer number showed a continuous film growth for the multilayer film. The POM’s W-O II oxidation peak showed up to 4
times an increase in surface coverage up to 0.2 nmol cm$^2$, whereas the RuD’s Ru(III/II) oxidation peak gave 6 times an increase in coverage upon layer formation. The constructed films showed significant stability towards both redox cycling and long term storage in pH 2 buffer. For example, after 500 redox cycles there was in general a 5% decrease in peak currents associated with the film’s redox processes. This effect illustrate a good balance of charges for both $P_8W_{48}Fe_{16}$ and RuD leading for high stability of LBL deposits [31].

Immobilisation by the LBL technique led to changes in the $P_8W_{48}Fe_{16}$ cyclic voltammogram. The potentials of both W-O redox processes were slightly changed with respect to the solution behaviour of the POM. The I and II W-O reduction peaks observed with the LBL film-modified electrode merged into a single broader peak at higher layer number. This result is different from the LBL deposition of the lacunary species $P_8W_{48}$, where wave splitting between the redox processes I and II was observed [34]. The oxidation peak of the 16 iron centres was shifted in comparison with its solution behaviour from +0.54 V to +0.70 V and was seen to grow with increasing layer number, whereas its peak potential shifted anodically.

Scan rate studies for the multilayer film showed diffusion control for the W-O II redox process up to 5 V s$^{-1}$ for an LBL film composed of 20 layers, with either an outer POM or cationic layer. However the redox peak currents for the Ru(III/II) couple showed thin film behaviour up to 5 V s$^{-1}$ for films composed of either an outer POM or cationic layer. It was found that there was a linear trend between the peak separation and the square root of the scan rate for the Ru(III/II) redox process, which indicates that the redox process is quasi-reversible in nature [55].

The Fe(III/II) oxidation peak demonstrated thin film behaviour with no splitting up to 1 V s$^{-1}$ within a LBL film composed of either an outer POM or cationic layer. An anodic shift of the oxidation process was also observed with increasing scan rate which represents the slower electron transfer kinetics associated with this redox process in comparison with the I and II W-O and Ru(III/II) redox processes. The Fe (III/II) oxidation processes became diffusion controlled at scan rates higher than 1 V s$^{-1}$.  

10
3.2.2 Electrochemical Impedance Spectroscopy (EIS)
EIS studies have been carried out during the growth of the POM-RuD assemblies after the deposition of each anionic and cationic layer. Figure 4 illustrates the resulting impedance spectra obtained at various stages of film growth, in the form of a Nyquist plot. The previous Randles equivalent circuit [53] has been employed to allow interpretation of the resulting plots. This model consists of a double layer capacitance in series with a solution resistance and in parallel with a diffusional branch, i.e. Warburg impedance and charge transfer resistance. The constant phase element was introduced instead of the double layer capacitance, which illustrates the non-uniform distribution of capacitance over the electrode surface. Fitting of the resulting data showed up to a four orders of magnitude increase in the measured charge transfer resistance value, $R_{ct}$, with increasing layer number (Inset B of Fig. 4). It has been observed that the $R_{ct}$ increase with increasing assembly number can be described with a single exponential function up to 9 layers for the LBL film. This behaviour is probably due to the coherent electron tunnelling across the LBL film [56], which controls the electronic communication between the ferri/ferrocyanide redox couple and the underlying electrode surface. It can be expressed in terms of the tunnelling decay constant $\beta$ [56, 57]: 

$$R_{ct} = R_{ct}^0 \exp(\beta x),$$

where $R_{ct}^0$ is the factor depending on the redox probe and electrode surface properties. Higher assembly numbers (higher than 9) are characterised by deviation from the exponential function probably due to formation of non-homogeneous LBL films. The slope obtained from Inset B of Figure 4 gives the decay constant $\beta$ approximately to 0.5 per layer for the LBL assembly. The decay constants measured for thiols immobilised at gold surfaces and normalized by a methylene unit are up to two times higher than obtained here [51]. Taking into account the fact, that individual layers of the LBL assembly are likely much larger than one methylene unit of thiols, one can conclude that a smaller decrease in the electron-tunnelling probability with a length of a spacer is observed here.

3.2.3 Permeability of LBL films towards different redox probes
The porosity and permeability of the multilayer assemblies was investigated by studying the voltammetric responses of two well-known standard anionic and cationic
redox probes at the modified electrodes. The probes undergo reversible monoelectronic redox processes at the bare electrode surface (anionic $[\text{Fe(CN)}_6]^{3/4-}$: $E_{1/2}$ of +0.21 V (vs Ag/AgCl); cationic $[\text{Ru(NH}_3)_6]^{3+/2+}$: $E_{1/2}$ -0.16 V (vs Ag/AgCl)). Upon contact with the modified multilayer electrode the probes can undergo the redox process at the underlying electrode surface after diffusion through the multilayer system or at the film|solution interface by electron transfer mediation by the redox sites within the LBL film [48]. The electrode modification with LBL films of different assembly numbers and outer layers showed a sufficient decrease in the anionic probe’s voltammetric signal with the response becoming sigmoidal in shape (e.g. Fig. 5A), thereby indicating the presence of “pin-hole diffusion” [25]. The repulsion between the anionic layers of the film and the anionic redox probe leads to decreases in the redox currents [58], which cannot be compensated by the introduction of the cationic layers of the RuD moiety. The increase in layers led to further probe response suppression or complete loss of permeability for the anionic redox probe for the LBL film after deposition of the cationic layer. The LBL deposition of 10 and 11 layers led to partial suppression of cationic probe’s response, whereas thicker films revealed a complete loss of permeability for the cationic probe. The plateau shape of the probe response at low layer numbers indicates the presence of pin hole or hindered diffusion within the LBL assembly [27]. Thus both the thickness of the LBL films and the nature of the terminal layer have an effect upon the film’s permeability.

3.2.4 Electrochemical kinetics of the ferri/ferrocyanide couple at the LBL film modified electrode

Investigations into the effect of modifying the carbon electrode surface with multilayer films composed of POM and RuD moieties upon the standard heterogeneous charge transfer rate constant, $k^0$, for the $[\text{Fe(CN)}_6]^{3/4-}$ redox system have been undertaken. Cyclic voltammograms of $[\text{Fe(CN)}_6]^{3/4-}$ were recorded with scan rates between 10mV/s and 5 V/s at varying stages of multilayer construction. The ratio of the anodic (Ipa) and cathodic (Ipc) peak currents and the $\Delta E_p$ values as a function of scan rate were measured. The deposition of a positively charged PDDA (layer 4) layer and the first RuD layer (layer 3) led to a decrease in the peak
separation to the values expected for a reversible one-electron process of a freely diffusing species. The deposition of the POM layers led to quasi-reversible voltammetric responses for the redox probe. The linear behaviour between the measured $\Delta E_p$ and the square root of the scan rate as evidence for the presence of a quasi-reversible redox process [55] has been observed at all steps of LBL assembly construction except during deposition of the 6th layer. The $I_{PA}/I_{PC}$ values were very close to unity, giving a transfer coefficient close to 0.5. Under these conditions it is possible to study the kinetics of the electrode reaction, with the separation of the peak potentials, $\Delta E_p$, being a measure of the standard rate constant for electron transfer [59]. These $\Delta E_p$ values were introduced in the working curve described by Nicholson [55] for obtaining the transfer parameter, $\Psi$, which is then employed to elucidate the standard heterogeneous charge transfer rate constant for the electron transfer process according to the following equation [60]:

$$\Psi = \frac{\left(\frac{D_O}{D_R}\right)^{\alpha/2} k^0}{\sqrt{D_O \pi \nu m F / R T}}$$

(1)

where $\nu$ is the scan rate, $\alpha$ is the transfer coefficient, $k^0$ is the standard rate constant (cm s$^{-1}$), $D_O$ and $D_R$ are the diffusion coefficients of the oxidised (7.3x10$^{-6}$ cm$^2$ s$^{-1}$ [61]) and reduced (6.7x10$^{-6}$ cm$^2$ s$^{-1}$ [61]) species for the redox probe, respectively. $\Psi$ was calculated at each sweep rate from the peak potential separation, and $k^0$ was calculated from the linear regression of the dependence of $\Psi$ on $\nu^{-1/2}$ (eq. 1). The heterogeneous charge transfer rate constant was in between 3x10$^{-4}$ – 3x10$^{-2}$ cm s$^{-1}$ and dependent on the LBL assembly number (Fig. 5B). It is clearly shown, that the kinetics of electron transfer between LBL film and aqueous redox couple is affected by the surface termination. Due to electrostatic interactions the deposition of positively charged molecules such as PPDA and RuD enhance the rate of heterogeneous electron transfer. On the contrary, $P_8W_{48}Fe_{16}$ terminal layers showed up to 25% decrease of heterogeneous rate constant. The same behaviour has been observed with LBL films based on Cu$^{2+}$- and Co$^{2+}$-substituted Krebs-type polyoxometalates and RuD [62].
3.2.5 Electrocatalytic properties of $P_8W_{48}Fe_{16}$-RuD LBL films

Polyoxometalates have previously been employed for the reduction of nitrite [62] and hydrogen peroxide [34, 63, 64]. Here the electrodes modified with LBL films with both outer layers were investigated for the electrocatalytic reduction of nitrite and hydrogen peroxide. Figure 6 shows the series of cyclic voltammograms recorded at an electrode modified with a $P_8W_{48}Fe_{16}$-RuD LBL film in pH 2 buffer in the absence and presence of various concentration of nitrite and hydrogen peroxide. In agreement with the electrocatalytic activity of $P_8W_{48}Fe_{16}$ studied in solution the W-O I redox process is not affected by the presence of the substrates, whereas the cathodic peak current of the W-O II redox process increased, accompanied by a decrease in it’s anodic counterpart’s peak current. The same behaviour was observed with films of different assembly numbers upon the addition of the analytes at pH 2 and 4.5 (data not shown). As with the solution behaviour the $P_8W_{48}Fe_{16}$-RuD LBL films revealed excellent selectivity towards nitrite reduction. The analytical performance of the layers for both nitrite and peroxide detection has been assessed under different experimental conditions by voltammetry. Immobilisation of the POM catalyst by means of LBL onto electrode surface led to a decrease in the sensitivity. The films of higher assembly numbers showed higher sensitivities, but shorter linearity regions. This effect illustrates the increase of electrocatalytic material load accompanied by the increase of diffusion impediment for substrate molecules at higher assembly numbers. Calibration plots for peroxide detection have two regions of linearity possibly due to local pH changes caused by formation of OH$^-$ as a product of peroxide reduction.

The comparison of performance characteristics of $P_8W_{48}Fe_{16}$-RuD LBL films with analytical parameters of systems known from literature (Table 1) shows that in the most of the cases the elaborated LBL assembly has a better characteristics especially for nitrite detection at pH4 and in comparison with other LBL films.

3.1 Surface analysis

3.1.1 XPS
Surface composition of the LBL films deposited on ITO glass slides, determined by XPS, which has a probe depth of approximately 10 nm, confirms the presence of Fe, P, W, O, Ru, C and N within the multilayer assembly. The presence of these elements is shown in the survey spectrum (data not shown). The presence of the POM is evident from the Fe 2p doublet peak at binding energy of ~ 710 eV, W 4f doublet at 35.3 eV and P 2p at 133.4 eV. High resolution spectrum of C 1s (not shown) can be decomposed mainly into peaks that are representative of C=C (284.8 eV), C-O/C-N (286 eV) and shake-up satellite peaks from unsaturated bonds (292.5 eV). In addition, the related N 1s peak at 400 eV and Ru 3d at 281 eV confirm the presence of pyridine based Ru dendrimer layer. Other elements present in the LBL films could not be identified as they may be present in concentrations below the detection limit of the instrument (~ < 0.1 atomic %).

3.1.2. AFM

AFM was conducted at different stages during the construction of the LBL assembly so as to examine the resulting changes in the topography of the multilayers. Figure 7 illustrates the evolution of the surface topography from the bare slide (Fig. 7A), through deposition of one PDDA layer (Fig. 7B) followed by the first POM layer (Fig. 7C) and after the deposition of the film through 17 assembly steps with the POM (Fig. 7D) or with RuD (Fig. 7E) as the terminal layers. Upon depositing the initial PDDA layer on the ITO substrate (Fig. 7B), the polymer filled in the low-lying valleys on the ITO surface, but followed the contours of the high features on the substrate, resulting in an overall increase in $S_q$, the root mean square height of the surface, consistent with the mechanism proposed by Zynek et al (cf. Fig. 4 [31]). Addition of a first $P_8W_{48}Fe_{16}$ layer (Fig. 7C) significantly reduced $S_q$ and yielded a homogenous surface topography. Following further deposition of the LBL film of 16 assembly steps, globular structures were observed. These globules were of similar shape and distribution for films with different terminal layers (Fig. 7D and 7E). However, the associated change in $S_q$ was 5 times smaller for a $P_8W_{48}Fe_{16}$ terminal layer than for a RuD (3.51 nm vs. 15.9 nm) terminal layer. These observations suggest that, the negatively charged POM preferentially fills in the low-lying valleys on the surface, whereas the cationic RuD and PDDA layers agglomerate, resulting in increased
with respect to the underlying surface. These observations are in agreement with data reported previously [31, 65]. Little phase contrast was seen for all the layers analysed; this suggests that the samples consisted of a homogeneous film within the areas of interest imaged.

3.1.3. SEM
SEM confirmed the coverage of the POM across the substrate. As can be seen in Figure 7F, the POM layer is relatively flat. The grains of the coating vary from string-like morphology (200 nm in diameter and 500-800 nm in length) to spherical grains of ~100 nm in diameter. EDS supported the XPS data on the presence of Fe and W (data not shown). Due to the higher penetration depth of the beam, compared to XPS, the signal from these elements were very low, which is likely to account for the absence of P and Ru (which is in a lower percent than Fe and W). The EDS spectra were plotted on a Log scale in order to observe the small peaks.

Conclusions
The iron-substituted crown-type polyoxometalate $P_8W_{48}Fe_{16}$ has been successfully immobilised onto carbon electrodes through the employment of the LBL technique utilising a Ru(II)-metallodendrimer as the cationic layer within the assembly. The resulting films showed clear well behaved redox activity for both the POM and the metallodendrimer moieties. Films exhibited thin layer behaviour up to 5 $Vs^{-1}$ and excellent stability towards redox cycling. The permeability of the films was found to be dependent upon the film’s thickness and the nature of it’s outer layer. Resulting films exhibiting enhanced electrocatalytic activity towards both nitrite and hydrogen peroxide reduction. The uniform nature and morphology of the LBL films was evidenced by the application of AFM.
References

Table 1. Analytical characteristics of different electrocatalytic systems based on POMs.

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>Sensitivity mA/(M cm²)</th>
<th>Linearity from – to (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nitrite at low pH</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P₈W₄₈Fe₁₆ in solution</td>
<td>2</td>
<td>25⁺</td>
<td>0.2 – 10</td>
</tr>
<tr>
<td>11 steps of LBL assembly</td>
<td>2</td>
<td>4.5⁺</td>
<td>0.2 – 10</td>
</tr>
<tr>
<td>21 steps of LBL assembly</td>
<td>2</td>
<td>13⁺</td>
<td>0.2 – 8</td>
</tr>
<tr>
<td>K₇[H₄PW₁₈O₆₂]-PAH LBL film [66]</td>
<td>1.2</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>K₆P₂W₁₈O₆₂-PAMAM LBL film [18]</td>
<td>1.1</td>
<td>2.9</td>
<td>0.1 – 30</td>
</tr>
<tr>
<td>H₆P₂Mo₁₈O₆₂-based composite with ordered mesoporous carbon [67]</td>
<td>0</td>
<td>41</td>
<td>0.05 – 24</td>
</tr>
<tr>
<td>W/WO₃ electrode [68]</td>
<td>0.7</td>
<td>370</td>
<td>1.6 – 20</td>
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<tr>
<td>(Bu₄N)₃SiW₉O₂₇(C₅H₅-Ti)₃-doped composite [69]</td>
<td>0.7</td>
<td>9.4</td>
<td></td>
</tr>
<tr>
<td>[SiW₁₂O₄₀]⁺ [70]</td>
<td>0</td>
<td>183</td>
<td>1-8</td>
</tr>
<tr>
<td>[SiW₁₂O₄₀]⁴⁺ [70]</td>
<td>0</td>
<td>70</td>
<td>0.5-10</td>
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<tr>
<td><strong>Nitrite at pH 4.5</strong></td>
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<td></td>
<td></td>
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<tr>
<td>P₈W₄₈Fe₁₆ in solution</td>
<td>4.5</td>
<td>72⁺</td>
<td>0.2 – 10</td>
</tr>
<tr>
<td>11 steps of assembly</td>
<td>4.5</td>
<td>22⁺</td>
<td>0.2 – 10</td>
</tr>
<tr>
<td>21 steps of assembly</td>
<td>4.5</td>
<td>38⁺</td>
<td>0.2 – 3</td>
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<tr>
<td>K₃[SiW₁₁Fe(H₂O)O₃₉]-PEI LBL film [36]</td>
<td>4</td>
<td>6</td>
<td>up to 0.7</td>
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<tr>
<td><strong>Hydrogen peroxide</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P₈W₄₈Fe₁₆ in solution</td>
<td>2</td>
<td>11.7⁺</td>
<td>0.2 – 10</td>
</tr>
<tr>
<td>11 steps of LBL assembly</td>
<td>2</td>
<td>5.6⁺</td>
<td>0.2 – 5</td>
</tr>
<tr>
<td>21 steps of LBL assembly</td>
<td>2</td>
<td>8.8⁺</td>
<td>0.2 – 6</td>
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<tr>
<td>K₆P₂W₁₇VO₆₂-based composite [71]</td>
<td>0</td>
<td>10.7</td>
<td>0.2 – 30</td>
</tr>
<tr>
<td>H₃PMo₁₂O₄₀-doped PPy with carbon paste [23]</td>
<td>0</td>
<td>15.6</td>
<td>0.1 – 20</td>
</tr>
<tr>
<td>H₆P₂Mo₁₈O₆₂-based composite with ordered mesoporous carbon [67]</td>
<td>0</td>
<td>1.5</td>
<td>0.16 – 44</td>
</tr>
<tr>
<td>H₃[PMo₁₂O₄₀]-[Ru(bpy)₃]Cl₂-composite [72]</td>
<td>0</td>
<td>0.3</td>
<td></td>
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</table>

* assessed at low concentrations of calibration plot in linear coordinates
Figure legends

**Figure 1.** A: Combined polyhedral/ball-and-stick representation of the [P₈W₄₈O₁₈₄Fe₁₆(OH)₂₈(H₂O)₄]²₀⁻ POM Color code: Fe (brown), O (red), PO₄ tetrahedra (pink), WO₆ octahedra (teal). B: Structure of the ruthenium (II) pentaerythritol-based metallodendrimer.

**Figure 2.** Electrochemical properties of P₈W₄₈Fe₁₆ in solution. (A) Insertion of Fe³⁺ ions into the precursor. Cyclic voltammograms of Fe³⁺-substituted POM P₈W₄₈Fe₁₆ (0.25 mM) and its precursor [P₈W₄₈O₁₈₄]⁴₀⁻ (0.25 mM) in aqueous pH buffer at a glassy carbon electrode (A=0.0707cm²). Scan rate 10 mVs⁻¹. Electrocatalytic reductions of sodium nitrite (B) and hydrogen peroxide (C) by P₈W₄₈Fe₁₆ in solution. Cyclic voltammograms were obtained at the bare GCE in 40 mM P₈W₄₈Fe₁₆ solution (pH2) in absence (solid line) and presence of analytes (dashed lines; B – sodium nitrite, C – hydrogen peroxide): 1, 2, 3, 4 and 5 mM. Scan rate 2 mVs⁻¹. Insets: calibration plots for nitrite and peroxide detection.

**Figure 3.** Consecutive cyclic voltammograms obtained at a GCE electrode modified with of LBL films with POM terminal layers (A) and RuD terminal layers (B). C – dependences of peak charges on layer number (☐ - RuII/III redox peaks; ■ - W-O II redox peaks). Scan rate 2 mVs⁻¹, pH 2.

**Figure 4.** Assembly of P₈W₄₈Fe₁₆-RuD LBL-films monitored by impedance spectroscopy. Nyquist plot of impedance spectra recorded at GCE electrode modified with P₈W₄₈Fe₁₆-RuD LBL films (1 - spectrum of blank electrode; 2 - spectrum of PDDA-modified electrode; 3 and 5 - spectra of modified electrode after first and second ‘POM’ steps; 4 - spectra of modified electrode after ‘binder’ step) in redox probe (10 mM K₃[Fe(CN)₆], 10 mM K₄[Fe(CN)₆], 0.1M KCl); 10mV amplitude, 230 mV potential of measurement. Insets: A - high frequency plot; B - the dependence of fitted values of charge transfer resistance on the assembly numbers.

**Figure 5.** Permeability of films by redox probes. Cyclic voltammograms were recorded at electrode modified with LBL film of 11 steps (POM terminal layer) in
pH2 buffer before (thin line) and after (thick line) addition of 1 mM K₃[Fe(CN)₆] (A) or 1 mM [Ru(NH₃)₆]Cl₃ (B). Dashed line – voltammograms of redox probes at blank GCE. Scan rate 10 mV/s, pH2. C - the dependence of heterogeneous charge transfer rate constant of [Fe(CN)₆]³⁻/⁴⁻ redox process on the assembly numbers of P₈W₄₈Fe₁₆-RuD LBL films attached to GCE electrode.

**Figure 6.** Electrocatalytic properties of P₈W₄₈Fe₁₆-RuD LBL films. Cyclic voltammograms were obtained with GCE modified by LBL film of 21 assembly steps with POM terminal layer in absence (solid line) and after additions of sodium nitrite (A) and hydrogen peroxide (B) (dashed lines: 0.4, 1, 2 and 3 mM). Scan rate 2 mVs⁻¹, pH2. Insets: calibration plots.

**Figure 7.** Evolution of topography observed during the LBL film assembly. The AFM images have been obtained at different stages of assembly at ITO-coated glass slide. A – bare slide, B – slide with deposited PDDA layer, C – PDDA-modified slide after deposition of first P₈W₄₈Fe₁₆ layer, D - slide modified with LBL film of 19th assembly steps with P₈W₄₈Fe₁₆ terminal layer, E - slide modified with LBL film of 19th assembly steps with RuD terminal layer. F - SEM image of slide modified with LBL film of 19th assembly steps with P₈W₄₈Fe₁₆ terminal layer.
R. Naseer et al., Figure 1.
R. Naseer et al., Figure 2
R. Naseer et al., Figure 3
R. Naseer et al., Figure 4
R. Naseer et al., Figure 5
R. Naseer et al., Figure 6
R. Naseer et al., Figure 7