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Polyoxometalates as solution-phase electrocatalytic mediators for reduced electrode fouling and the improved oxidative response of phenols

Md. Mokarrom Hossain, Leigh Aldous *

School of Chemistry, UNSW Australia, Sydney, NSW 2052, Australia

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ABSTRACT

The electrochemical oxidation of phenols typically passivates electrodes, due to the reactive one-electron oxidation intermediate, a phenoxyl radical cation. Here, we show that the addition of polyoxometalates to the electrolyte can prevent electrode passivation via an EC`E mechanism; the initial oxidation is unchanged, but oxidation of the phenoxyl radical intermediate is mediated. As such the electrochemistry assumes an ideal EE process, as confirmed by cyclic voltammetric simulation, with no electrode fouling on the voltammetric timescale. Bulk electrolysis of phenolic molecules can even be performed to isolate solution-phase products. This is exemplified by the scenario of vanillin (phenolic compound) and phosphotungstic acid ($H_3[PW_{12}O_{40}]$, a polyoxometalate).

1. Introduction

Phenolic compounds are widely present in environmental matrices, as phytochemicals, industry by-products, *etc.* [1]. Many phenols are protoplasmic poisons, known to damage a range of organs [2]. Several phenolic compounds are considered priority pollutants; their identification and quantification are extremely important for environmental monitoring [3]. Conversely, many phenols are also potent and important flavour and fragrance molecules, and their quantification is important for quality control, electronic noses, *etc.* [4]. Vanillin, a phenolic aldehyde, is a key example of a flavour and fragrance molecule that is both found in natural systems and is produced on a massive industrial scale for human consumption.

Chromatography, spectrophotometry and capillary electrophoresis have all been utilised for the quantification and identification of phenolic compounds [5]. However, these techniques involve complicated, time-consuming sample preparation; instruments are usually bulky and require long analysis times, which make them inconvenient for in-field or routine analysis. In contrast, electrochemical techniques can offer a wide range of benefits such as simplicity, rapidity, high sensitivity, reliability and portability, which make them ideal for monitoring environmental pollutants [6].

Typically the electrochemical oxidation of phenols results in electrode fouling; the one-electron oxidation product is a phenoxyl radical which adsorbs, reacts with or polymerises on the electrode surface [7] even in exotic electrolytes such as ionic liquids [8]. This results in poor sensitivity and necessitates disposable, cleanable or anti-fouling electrodes [9,10]. Several electrode-focussed approaches have been reported, such as modifying the electrode surface with functional materials [5], using boron-doped diamond films [11], screen printed carbon electrodes [12], Nafion films [13], conducting polymer film modified electrodes [2], and enzyme-coated electrodes [3]. Enclosed systems such as microfluidic chips have to resort to chemical removal of phenolic passivating films [14].

When the redox electrochemistry of an analyte is thermodynamically feasible but kinetically limited at an electrode surface, solution phase 'electrocatalytic' mediators can be added. They typically have favourable electrochemistry, and the voltammetry of the mediator directly reflects the concentration of the analyte [15]. A few papers report the 'indirect' quantification of phenolic species: *e.g.* Lowe et al. electrochemically oxidised 2,6-dichloro-*p*-aminophenol, which then reacted with phenols to form voltammetrically detectible quinone species [16]; Kolliopoulos et al. electrochemically oxidised phenols at boron-doped diamond electrodes, which reacted stochiometrically with pyrazoline derivatives to form voltammetrically detectible quinone species [17]; and Del Carlo et al. complexed *o*-diphenols with molybdate for the improved quantification of diphenols in olive oil [18].

* Corresponding author.
E-mail address: l.aldous@unsw.edu.au (L. Aldous).

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Polyoxometalates (POMs) are polyatomic ions which contain transition metals joined into a 3D framework by multiple oxygen atoms [19]. POMs are widely available with different dimensions, charge density, shape, reactivity and multiple redox features [19]. POMs have been utilised as stoichiometric chemical oxidants for different organic compounds, including phenolic compounds [19]. POMs have also been utilised as electrocatalytic mediators [20], although not in conjunction with phenols.

In this study, we have demonstrated that the conventional electrode-fouling voltammetry for phenolic compounds can alter to ideal voltammetry upon addition of a suitable POM. Electrode fouling is suppressed and exhaustive bulk electrolysis can even be performed, allowing isolation of the solution-phase (electro)oxidised phenol product.

2. Experimental

Milli-Q water (18.2 MΩ cm^{-1}) was used to prepare all the aqueous solutions. Vanillin, *para*-cresol, dopamine hydrochloride and 3,4-dihydroxybenzaldehyde (all from Sigma-Aldrich), guaiacol (Chem Supply) and 2,4-dihydroxybenzaldehyde (Lancaster) were used as received.

The POMs STA ($H_4[SiW_{12}O_{40}]$), Sigma Aldrich), PMA ($H_3[PMo_{12}O_{40}]$, Sigma-Aldrich) and PTA ($H_3[PW_{12}O_{40}]$, Fluka) were purchased and used as received. The POMs PVM ($H_5[PV_2Mo_{10}O_{40}]$) [21], PVW ($K_4[PVW_{11}O_{40}]$) [22], SiVW ($K_5[SiVW_{11}O_{40}]$) [23] and BVW ($K_7[BVW_{11}O_{40}]$) [24] were prepared according to the reported literature methods.

All cyclic voltammetry (CV) experiments were performed using a glassy carbon working electrode (GC, 3 mm diameter), Pt counter and Ag|AgCl reference electrode (all BASi Analytical, USA) using an Autolab PGSTAT101 (Ecochemie, the Netherlands). A 100 mV s^{-1} scan rate was used for all the experiments. Bulk electrolysis experiments used a GC bulk electrode (SIGRADUR G, HTW, Germany), using a separate electrode compartment for the counter electrode (BASi Analytical, USA). Electrochemical simulation was performed using DigiElch7 software.

3. Result and discussion

As our results are exemplified by the case of vanillin (phenolic compound) and phosphotungstic acid (PTA, $H_3[PW_{12}O_{40}]$, a polyoxometalate), this system will be discussed in detail. A wider range of phenolics and polyoxometalates are briefly described at the end.

Fig. 1(a) displays a cyclic voltammogram (CV) of vanillin at a glassy carbon (GC) electrode. A broad peak is present at *ca.* +0.95 V (*vs* Ag|AgCl) on the first scan, due to the oxidation of vanillin. For the second and successive scans, the oxidation peak decreased dramatically, and no corresponding reduction features were observed. This is indicative of electrode fouling by the oxidised vanillin, due to the one electron formation of a cationic phenoxyl radical [7,25]. Enache and Oliveira-Brett have shown that the peak current for the oxidation of phenol in aqueous H_2SO_4 does not scale with concentration due to electrode fouling [10]; the Randles–Sevcik equation for the system in Fig. 1 also predicts a peak current value *ca.* 10-fold higher (*vide infra*). This indicates significant passivation early within the first scan. Assuming vanillin is a sphere with *ca.* 1 nm diameter, a densely packed monolayer would consist of *ca.* 1.3×10^{14} molecules cm^{-2}. In the 40 mM vanillin solution, this quantity of vanillin is present within the first *ca.* 50 μm directly adjacent to the electrode surface; diffusion layers larger than 100 μm are expected for CVs at 100 mV s^{-1} in aqueous electrolytes.

The voltammetry of PTA was also investigated (Fig. 1(a)). Scanning oxidatively from the open circuit potential, no Faradaic features were observed, indicating that the POM was already present in its most oxidised state ($[PW_{12}O_{40}]^{3-}$). On the reverse scan, two distinct reversible one-electron processes were observed (Fig. 1(a)), followed by a two-electron proton-coupled reduction and then multiple electron reductions (not shown, but consistent with the previously reported voltammetry for PTA) [20]. In 1 M H_2SO_4 PTA is fully dissociated, and the first two reductions do not include protonation [20].

The combination of 40 mM vanillin and 10 mM PTA in the same solution resulted in a significant change in the vanillin voltammetry. As shown in Fig. 1(c), an oxidative peak with *ca.* 10-fold higher peak current was observed for vanillin, and no evidence of any electrode passivation, even after multiple cycles. The oxidation of vanillin became chemically reversible, with an associated reduction feature at *ca.* +0.45 V. Lower concentrations of PTA resulted in lower current and some electrode fouling; more than 10 mM PTA did not further increase the peak current, demonstrating that the interaction between PTA and vanillin was catalytic (with respect to PTA) rather than stoichiometric. POMs can physisorb at GC surfaces from H_2SO_4 [20], but physisorption of PTA onto the GC electrode before transferring into a vanillin solution demonstrated vanillin voltammetry consistent with the absence of PTA. This demonstrates that the process is likely solution-based, rather than a layer of PTA at the GC acting as either mediator or physical anti-fouling layer.

Homogeneous two electron oxidation of vanillin will result in a carbocation via the one-electron phenoxyl radical intermediate [26]. The *ortho*-methoxy group can subsequently hydrolyse to yield 1,2-benzoquinone-4-carbaldehyde [26]. A similar process has already been established for the electro-oxidation of similar *ortho*-methoxy phenolic species, such as capsaicin oxidation [27,28]. Therefore the well-defined voltammetry in Fig. 1(b) was digitally simulated,

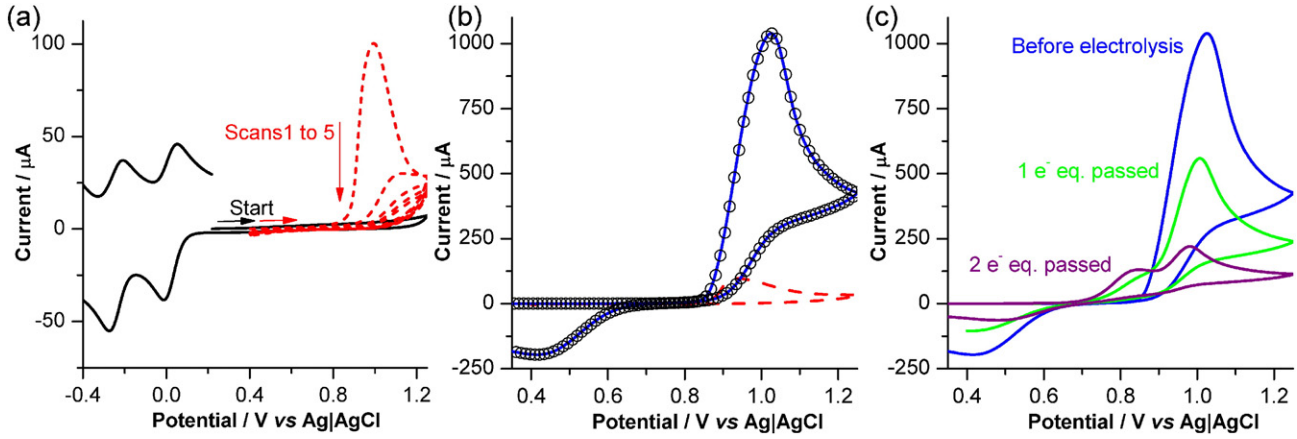

Fig. 1. Cyclic voltammograms in 1 M aqueous H_2SO_4 for (a) 40 mM vanillin for successive 5 scans (- - -) or 10 mM PTA (—); (b) 40 mM vanillin without (- - -) and with (—) 10 mM PTA; overlaid (o) is simulation for an EE mechanism; (c) 40 mM vanillin and 10 mM PTA before bulk electrolysis and after passing one e^- and two e^- per vanillin.