Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

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

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A B S T R A C T

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).

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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].

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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$_2$Mo$_{10}$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$_2$SO$_4$ 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$_2$SO$_4$ 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$_2$SO$_4$ [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,
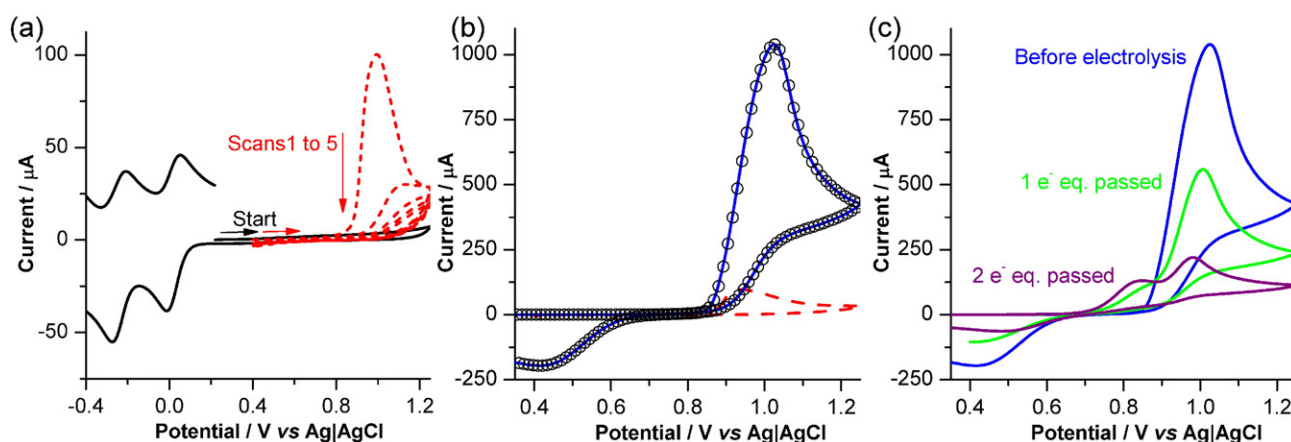

Fig. 1. Cyclic voltammograms in 1 M aqueous H$_2$SO$_4$ for (a) 40 mM vanillin for successive 5 scans (---) or 10 mM PTA (—); (b) 40 mM vanillin without (---) and with (—) 10 mM PTA; overlaid (o) is simulation for an EE mechanism; (c) 40 mM vanillin and 10 mM PTA before bulk electrolysis and after passing one e$^-$ and two e$^-$ per vanillin.

Table 1
Comparison of peak currents and peak potentials obtained from cyclic voltammograms for 40 mM of phenolic and non-phenolic compounds in the presence and absence of 5 mM PTA.

Compounds	I_p (µA)	I_p w/POM (µA)	Ratio I_p w/POM: I_p	E_p (V)	E_p shift w/POM (V)
Phenol	89	103 (5 mM)	**1.16**	1.02	**+0.01**
		190 (80 mM)	**2.13**		**+0.03**
Vanillin	95	650 (5 mM)	**6.82**	0.93	**+0.08**
		1050 (10 mM)	**11.1**		**+0.08**
p-Cresol	120	58	**0.48**	0.92	**−0.05**
Guaiacol[a]	215 (1st peak)	330 (one broad peak)	**1.53**	0.83	**+0.11**
	246 (2nd peak)			0.94	**+0.00**
2,4-Dihydroxy benzaldehyde	190	187	**0.98**	1.05	**+0.15**
Dopamine	554	39	**0.06**	0.64	**0.00**
Ascorbic acid	465	344	**0.74**	0.59	**+0.38**

[a] Irreversible peak became reversible upon addition of PTA.

assuming a simple EE oxidation of vanillin (two successive one-electron oxidation processes), and neglecting the presence of PTA. An excellent fit could be obtained from this simple model (Fig. 1(b)).

The Wilke–Chang equation [29] predicts a D of ca. 8.2×10^{-6} cm^2 s^{-1} for vanillin at 25 °C, and employing a D value of 8.12×10^{-6} cm^2 s^{-1} the excellent fit shown in Fig. 1(b) could be obtained for both the oxidative and reductive features. Identical values for the transfer coefficient ($\alpha = 0.42$), formal potential ($E^\circ = +0.755$ V) and heterogeneous rate constant ($k_s = 2.5 \times 10^{-5}$ cm s^{-1}) were used for both E processes.

The structure of PTA was retained in the presence of vanillin (confirmed colorimetrically and voltammetrically). The results indicate that the first electron oxidation of vanillin yields the cationic phenoxyl radical, which is thermodynamically unstable (i.e. $E^\circ \ll 0.7$ V) but kinetically stable with respect to oxidation at the electrode ($k_s \approx 0$), allowing polymerisation and side reactions to result in electrode fouling. In the presence of PTA, a homogeneous redox process could occur, the PTA oxidising the phenoxyl radical to the carbocation. The resulting reduced PTA is then rapidly re-oxidised at the electrode, accounting for its catalytic role. Therefore the formal mechanism will follow an EC`E process. However, as the homogeneous reaction and the oxidation of the PTA at >0.7 V are both so rapid it results in an apparent EE process.

An EE oxidation of vanillin requires that the final product be 1,2-benzoquinone-4-carbaldehyde. Therefore bulk electrolysis was performed using 40 mM vanillin in the presence of 10 mM PTA, in a divided cell. Electrical charge calculated to achieve the one electron and two electron oxidation of vanillin (19.3 C and 38.6 C, respectively, for 5 ml) was passed. Fig. 1(c) displays the CVs for the system before and after bulk electrolysis; the vanillin peak at +0.95 V decreased with increasing charge, and a new feature appeared at ca. +0.85 V. The electrolysis products were extracted from the reaction mixture with diethyl ether

and analysed using ^{1}H NMR and mass spectrometry. Both techniques identified the product as 3,4-dihydroxybenzaldehyde; the reduced form of 1,2-benzoquinone-4-carbaldehyde. An investigation of a commercial sample of 3,4-dihydroxybenzaldehyde confirmed its oxidation peak appears at ca. +0.85 V under the same conditions. Therefore, the two-electron oxidation of vanillin clearly occurs, in order to form the carbocation essential for the hydrolysis of the methoxy group. However, over extended durations only the reduced form of the oxidation product was isolated. In the electrolyte this reduction product was in turn electrochemically re-oxidised, and accounts for why only ca. 80% of the vanillin was consumed after passing two electron equivalents. Regardless, these preliminary results clearly demonstrate that, on the voltammetric time scale, the addition of PTA removes electrode-fouling and the system assumes essentially ideal voltammetric behaviour. Extended electrolysis to yield solution-phase products could be performed, which is not possible for vanillin in the absence of PTA. The presence of the POM and dissolved oxygen likely results in additional redox processes over longer time periods.

The wider applicability of this polyoxometalate-system towards phenols and electrode-fouling analytes was briefly investigated. Table 1 summarises the effect of adding PTA upon the voltammograms of phenol and substituted phenols. Vanillin underwent the most dramatic alteration; phenol could be improved but required more PTA. Conversely p-cresol was partially oxidised upon mixing with PTA, and the p-cresol peaks decreased over time. Other important electrode-fouling analytes such as dopamine and ascorbic acid [30,31] were spontaneously oxidised by the PTA.

The above results indicate that there is likely an optimum polyoxometalate for each analyte, with PTA being either too oxidising or not oxidising enough for analytes other than vanillin. To further investigate this hypothesis, a range of seven polyoxometalates were
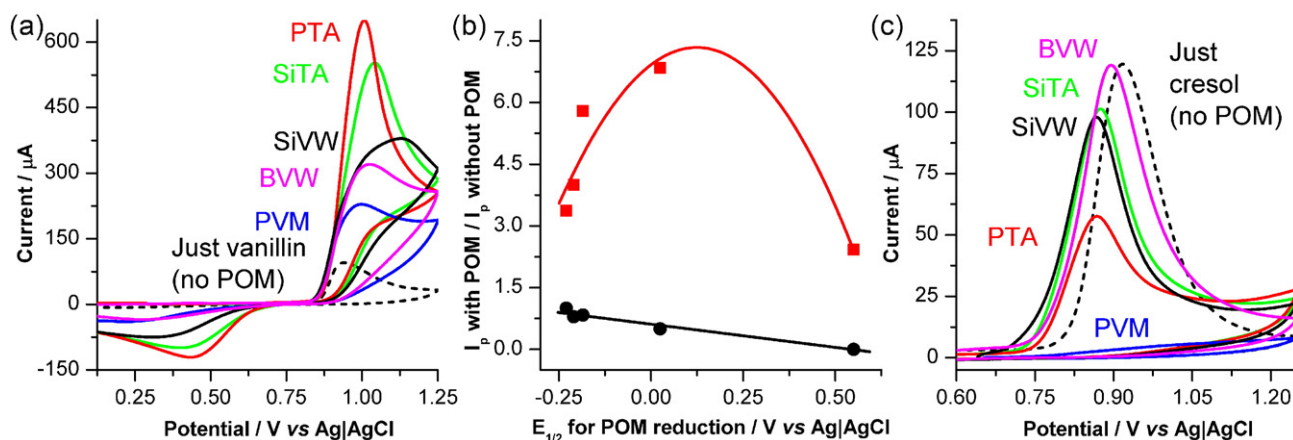
Fig. 2. Cyclic voltammograms in 1 M aqueous H$_2$SO$_4$ for (a) 40 mM vanillin and (c) 40 mM cresol in the absence (---) and presence (—) of 5 mM POM. Also plotted is (b) the ratio of the oxidation peak current with and without POM vs $E_{1/2}$ for the first POM reduction. The squares represent the vanillin data, and the circles represent the cresol data.

screened in conjunction with two phenols, vanillin and *para*-cresol. Full names of the POMs are listed in the experimental section. Five of the POMs displayed one-electron reversible reductions, with the $E_{1/2}$ at the indicated potentials (in 1 M H_2SO_4, *vs* Ag|AgCl); BVW (-0.23 V), SiVW (-0.21 V), SiTA (-0.19 V), PTA ($+0.03$ V) and PVM ($+0.55$ V). The POMs PVW and PMA displayed two-electron reductions and did not follow the same trends as the one-electron POMs, hence are not discussed further.

Fig. 2(a) displays CVs of 40 mM vanillin in the presence of 5 mM polyoxometalate. Generally, the more positive the reduction potential of the POM, the larger the current increase (Fig. 2(b)). The most oxidising POM investigated, PVM, was an exception and potentially oxidised some vanillin prior to the CV. This results in an apparent 'volcano curve' common to electrocatalysis [32].

The phenol *para*-cresol likely has a more negative formal potential than vanillin, as all POMs resulted in a reduction in the oxidation current relative to no POM (Fig. 2(c)). The more positive the reduction potential of the POM, the larger the current decrease (Fig. 2(b)), indicating that the optimum POM mediator would likely have a more negative reduction potential than those investigated here. The oxidation current also decreased over time, indicating on-going oxidation of the *para*-cresol. In particular, none of the 40 mM *para*-cresol remained after addition of 5 mM PVM, indicating the POM was a catalytic mediator and dissolved oxygen was likely the stoichiometric oxidising agent. Extraction of the solution and analysis by mass spectroscopy conclusively demonstrated the presence of *para*-cresol dimer as the predominate product. NMR analysis demonstrated multiple different dimers were present, due to phenoxyl radical formation followed by rapid solution-phase dimerization at various sites.

Notably, the redox properties of most phenols [10] and POMs [20] are strongly pH dependent – in different directions – and this represents another parameter for further optimisation of the mediation process.

4. Conclusions

This investigation has demonstrated that polyoxometalates can act as effective solution-phase mediators to encourage the (complete) two-electron oxidation of phenolic molecules. The thermodynamics of the oxidation of the phenolic molecule remain largely unchanged, but certain polyoxometalates are able to rapidly oxidise the phenoxyl radical intermediate. The polyoxometalate is re-oxidised, and acts as an (electro)catalytic mediator. The overall mechanism is thus an EC̀E process. Correct choice of polyoxometalate and phenolic analyte can result in essentially ideal diffusional two-electron oxidation voltammetry of the phenol, with no passivation of the electrode. The reduction potential of the polyoxometalate is essential in dictating the effectiveness of the polyoxometalate as a solution-phase mediator; if the polyoxometalate is too oxidising, consumption of the analyte can occur prior to electrochemical analysis.

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