

The Electro-Oxidation of Lactic Acid at Platinum Microparticles and Polycrystalline Platinum Electrode

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We report the electrochemical modification of boron-doped diamond electrode surface with electrodeposited platinum microparticles of mean size of 193 nm ± 107 nm. The activity of platinum microparticle modified boron-doped diamond (*ca.* 20 % platinum coverage) and platinum macro electrodes (100% platinum coverage) are measured and compared through lactic acid oxidation, selected because of the surface sensitive nature of the reaction. Significant differences are found with the modified BDD showing a markedly lower current density.

Keywords: platinum microparticles, lactic acid oxidation, boron-doped diamond, modified electrodes, polycrystalline platinum.

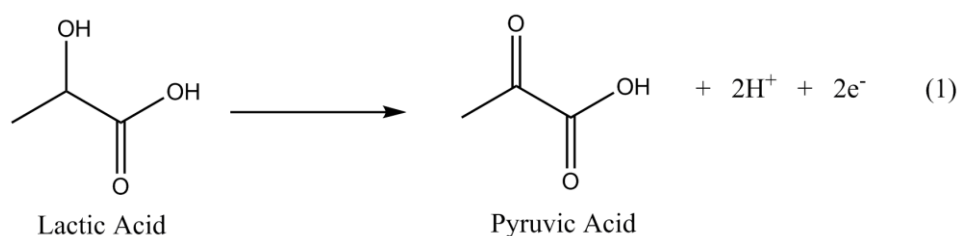
1. INTRODUCTION

Platinum is a precious metal that has great catalytic and electrical properties with superior corrosion resistance.[1] As of now, platinum is one of the known catalysts for alcohol electro-oxidation.[2-4] Thus, it has become widely adapted for applications such as in the direct alcohol fuel cell as well as in electrochemical sensors for different types of compounds such as glucose,[5, 6] carbon monoxide,[7,8] hydrogen peroxide,[9] arsenite,[10,11] ammonia,[12] and oxygen.[13] However, procuring bulk platinum is expensive for the industrial scale and / or commercialization. The current market price for platinum is \$ 1200 (US dollars per ounce).[14] In recent years, the study and

use of nano- or micro-structured particles have become popular due to their claimed ability to perform at similar standards to bulk platinum, less material lowering the cost.[2, 3, 15-17] However, the question arises as the extent to which these platinum microparticles quantitatively mirror the behaviour of bulk platinum electrodes.

Boron-doped diamond electrode (BDD) is a versatile electrode material with a wide range of application in electrochemistry. This is due to some features of diamond, such as high hardness, excellent durability, a relatively chemically inert surface, and a very high melting point.[18, 19] In addition, as electrode, BDD has low background current, wide potential window and good chemical and mechanical stability.[20] Other important characteristic of the BDD electrode is the non-uniform electroactivity across the surface, due to preferential accumulation of boron atoms at grain boundaries.[18, 21] Because of this BDD is a good support to formation of metallic particles and nanoparticles.[22]

Lactic acid is a naturally occurring organic acid that has a role in many biochemical processes. In biology, lactic acid, in the form of lactate, is produced from pyruvate during anaerobic respiration.[23] In industry, it has many applications in pharmaceutical,[24] cosmetic,[25, 26] food,[27, 28] and chemical industries[29-31] as a chemical promoter. In many ways, this compound containing small organic molecule is ubiquitous and converting it can be useful and important, especially in the industrial setting. According to The National Non-Food Crops Centre, 300,000 - 400,000 tonnes of lactic acid are produced per year in the world.[32] Electrochemical methods offer a fast and controllable way to facilitate the conversion of organic molecules into targeted fuel, bi-products, and / or products.[33-35] Currently, platinum metal is known to be a good catalyst for alcohol electro-oxidation for its lower overpotential and higher catalytic activity in comparison to all the other conventional electrodes (carbon, gold or diamond).[36-39] In particular, lactic acid can be electro-oxidised at a platinum electrode.[40-42] This reaction takes place via reaction with hydroxyl radical and involves the transfer of two electrons and formation of pyruvic acid, according to Equation 1.[40]



The reaction likely proceeds via surface adsorption so has been selected for study in this paper to address the question as to how closely platinum microparticles electrodeposited on BDD mirror the behaviour of bulk platinum.

2. EXPERIMENTAL PART

2.1. Reagents and solutions

Hexachloroplatinic (IV) acid ($\geq 99.9\%$, H_2PtCl_6) and lactic acid ($\geq 85\%$, $\text{C}_3\text{H}_6\text{O}_3$) were purchased from Sigma-Aldrich (Dorset, UK). Nitric acid (70%, HNO_3), hydrochloric acid (37%, HCl)

and sulphuric acid ($\geq 95\%$, H_2SO_4) were obtained from Fisher Scientific (Loughborough, UK). All solutions were prepared with deionised water from the Milli-Q system from Millipore[®] at a resistivity no less than $18.2 \text{ M}\Omega \text{ cm}$ at $25 \text{ }^\circ\text{C}$. H_2PtCl_6 solution and lactic acid stock solution of 0.50 mol L^{-1} were prepared in 0.50 mol L^{-1} sulphuric acid, which was employed as supporting electrolyte.

2.2. Apparatus

Electrochemical experiments were carried out using a potentiostat/galvanostat (AUTOLAB model PGSTAT 12, ECO-Chemie, NL) controlled by GPES 4.9 software. All experiments were carried out using a conventional single-compartment cell with three electrodes, the working electrode being a plate BDD, which was prepared by chemical vapor deposition technique by Element Six[®] (Didcot, UK) with an area of 1 cm^2 , boron concentration greater than 10^{20} cm^{-3} and resistivity of 0.02 to $0.18 \text{ }\Omega \text{ cm}$. The BDD was mounted in a home-built electrochemical cell so that only a circular area of 0.20 cm^2 was exposed to the electrolyte. A saturated calomel electrode (SCE) from BASi (West Lafayette, USA) and a graphite rod (Sigma-Aldrich, Dorset, UK) were used as reference and counter electrodes, respectively. A homemade platinum macro electrode set in PTFE with area of $3.40 \times 10^{-2} \text{ cm}^2$ was also used as working electrode. The temperature was controlled at $25 \pm 1 \text{ }^\circ\text{C}$ in all experiments.

2.3. Electrodeposition of platinum microparticles on BDD electrodes

Prior to the modification with platinum microparticles, the BDD electrode was cleaned in aqua regia ($3\text{HCl}:1\text{HNO}_3$) for 15 min and rinsed with deionised water. Afterwards, the electrode was polished with diamond spray (Kemet International, Maidstone, UK) in the sequence of 3.0 , 1.0 and $0.1 \text{ }\mu\text{m}$ particle size and sonicated in deionised water for 5 min. After BDD cleaning procedure, platinum microparticles were electrodeposited onto the BDD surface by electrochemical reduction in degassed 0.50 mol L^{-1} sulfuric acid solution containing 0.50 mmol L^{-1} H_2PtCl_6 . The BDD was held at -0.20 V (vs SCE) for 10 min. Platinum reduction is the main reaction which occurs during the electrodeposition process, therefore platinum loading can be calculated by electrodeposition charge. Under the deposition conditions employed above, platinum loading was calculated being $(19.2 \pm 2.3) \text{ }\mu\text{g cm}^{-2}$.

2.4. Platinum macro electrode

The platinum surface was polished with alumina powder (Buehler, Coventy, UK) in the sequence of 1.0 , 0.3 and $0.05 \text{ }\mu\text{m}$ particle size. It was then rinsed with deionised water and employed in the electrochemical measurements.

2.5. Characterization of the platinum particle modified BDD electrode

Scanning electron microscopy (SEM) and *energy-dispersive X-ray* (EDX) were used to characterize the platinum particle modified BDD electrode (Pt-BDD). The SEM analysis was performed on a scanning electron microscope (JEOL 6500F SEM) at an acceleration voltage of 10 kV and ImageJ software (National Institutes of Health, USA) was used to measure the particle size. For EDX analysis, a JEOL 6480LV SEM was used at an acceleration voltage of 15 kV with an Oxford Instruments Xmax 80 SDD X-ray detector. BDD electrode was modified as previously described, rinsed with deionised water and dried under nitrogen atmosphere prior to SEM and EDX analysis. In Figure 1a, a series of images at high and low magnifications of Pt-BDD electrode are shown. BDD surface was homogeneously covered by dispersed platinum microparticles. The histogram of diameter particle (Figure 1b) shows platinum microparticles with different sizes ranging from 40 to 490 nm (mean size of $193 \text{ nm} \pm 107 \text{ nm}$).

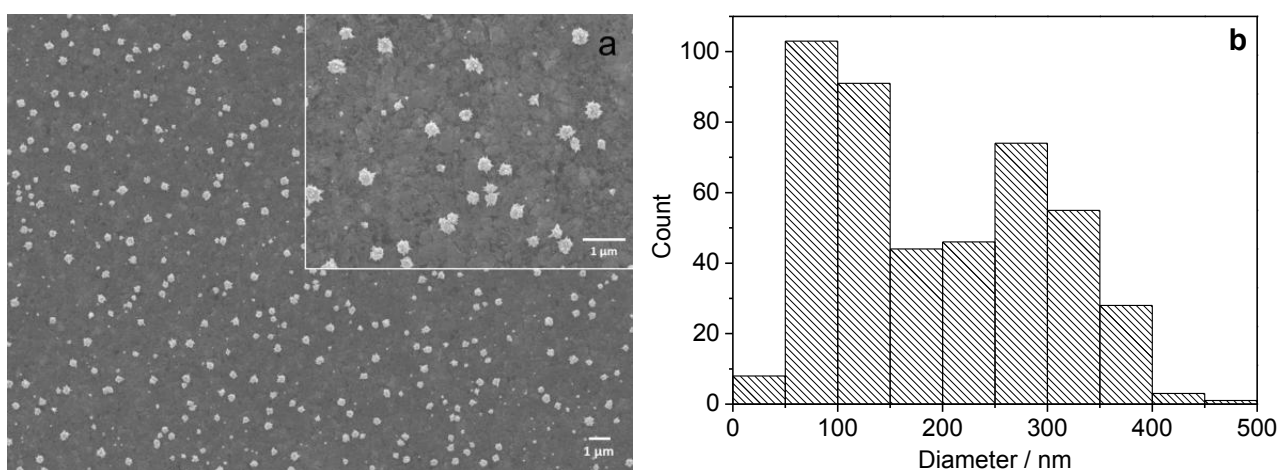


Figure 1. (a) SEM images of Pt modified BDD. BDD was modified at -0.20 V (vs SCE) for 10 min in degassed $0.50 \text{ mmol L}^{-1} \text{ H}_2\text{PtCl}_6$ in $0.50 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$. Inset: high magnification of Pt-BDD. (b) Histogram showing the size distribution of Pt microparticles.

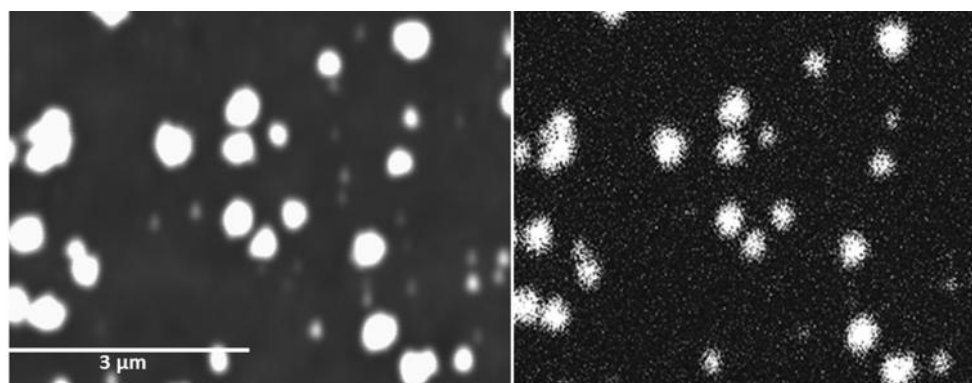


Figure 2. SEM image of Pt-BDD (a) and the corresponding EDX mapping of Pt (b).

Figure 2 shows the SEM image of the platinum modified BDD surface and its respective EDX mapping of platinum. From EDX mapping, platinum coverage was determined to be *ca.* 20 %. Figure 2b confirms the presence of platinum on BDD surface, through highlighted points. Numerous small platinum particles, which are not visually seen in the SEM image, can be detected by EDX. Therefore, these numerous small particles are not accounted in the size measurement via SEM, the actual average platinum size may be smaller than the measured value of $193 \text{ nm} \pm 107 \text{ nm}$.

3. RESULTS AND DISCUSSION

In this section, the Pt-BDD is first electrochemically characterised to investigate the deposition of platinum microparticles on BDD. Then, the voltammetric behaviour of Pt-BDD in the presence of different lactic acid concentrations is reported. The activity of Pt-BDD toward lactic acid oxidation is compared to a bulk platinum electrode. With this comparison, we are able to determine if a BDD partially covered with platinum microparticles is able to generate a comparable response to a bulk platinum electrode.

3.1. Electrochemical behaviour and characterization of the platinum modified BDD electrode

The BDD surface was modified with platinum microparticles, according to the procedure reported in experimental section.[4, 43, 44] After platinum particle electrodeposition, the modified BDD was placed in degassed $0.50 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution and undergone a potential cycle between -0.30 and $+1.65 \text{ V}$ (vs SCE) at 50 mV s^{-1} .

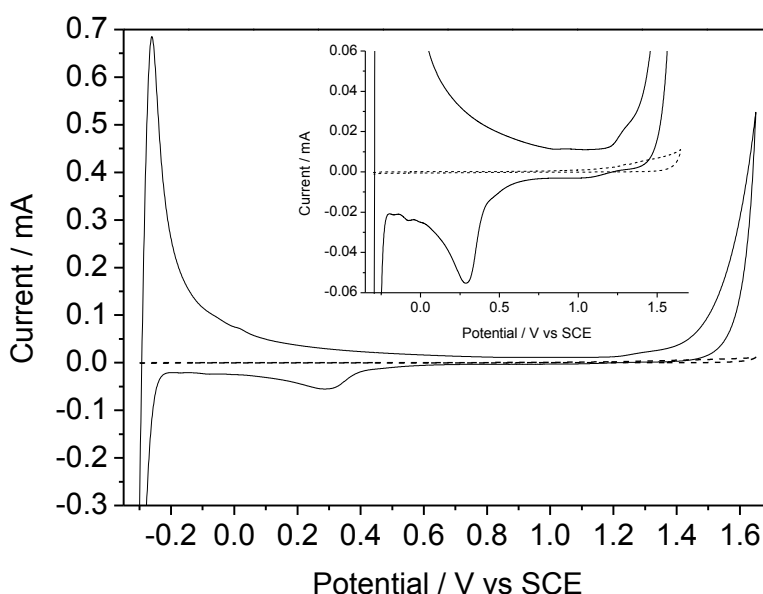


Figure 3. Overlay of cyclic voltammograms in degassed $0.50 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution at Pt modified BDD (solid line) and at unmodified BDD (dashed line) electrodes. Inset: zoom view. Scan rate: 50 mV s^{-1} .

In Figure 3, the cyclic voltammogram of Pt-BDD in the acidic medium (solid line) is plotted and compared to the unmodified BDD electrode (dashed line). In this potential window, bare BDD shows a very low capacitive current and there is an absence of faradaic processes. For Pt-BDD, the anodic and cathodic peaks observed at *ca.* -0.26 V (vs SCE) are attributed to hydrogen desorption and adsorption respectively.[45-47] The increase of anodic current at potentials larger than +1.25 V (vs SCE) is accounted by the formation of platinum oxide,[47] which is re-reduced to metallic platinum at *ca.* +0.29 V (vs SCE) in the backward scan.[4] All the voltammetric peaks observed corresponds to literature, suggesting that platinum microparticles were successfully electrodeposited on the BDD surface.[4, 12, 43, 46, 47]

3.2. Electro-oxidation of lactic acid at a Pt-BDD

Voltammetric behaviour of unmodified BDD in degassed 0.50 mol L⁻¹ H₂SO₄ solution in absence and in presence of lactic acid was studied (not shown). No change in cyclic voltammograms in presence of lactic acid, up to concentration of 0.10 mol L⁻¹, was observed. This indicates unmodified BDD is not able to oxidise this compound.

To determine the activity of Pt-BDD towards lactic acid oxidation, a potential cycle from -0.30 to +1.65 V (vs SCE) was applied in presence of different lactic acid concentrations. Figure 4a illustrates cyclic voltammograms recorded in degassed 0.50 mol L⁻¹ H₂SO₄ solution in presence of 0.50 mmol L⁻¹ to 50 mmol L⁻¹ of lactic acid at 50 mV s⁻¹. An increase in the anodic signal at *ca.* +1.35 V (vs SCE) is observed with increasing lactic acid concentration, indicating lactic acid electro-oxidation. As discussed in the introduction, this oxidation process involves a transfer of two electrons, to form pyruvic acid.[40] There is no corresponding cathodic peak observed, which indicates a chemically irreversible oxidation of lactic acid.[40]

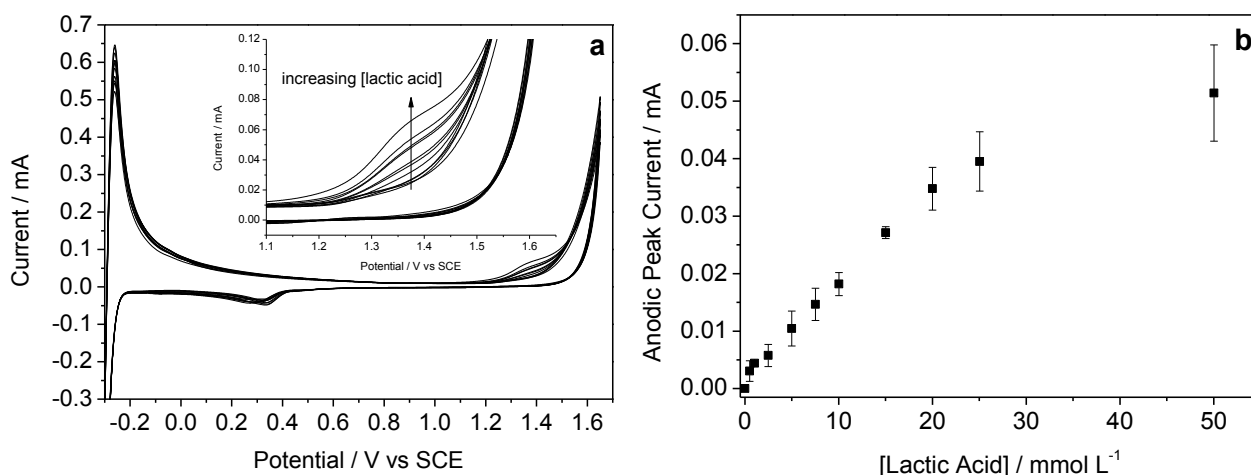


Figure 4. Overlay of successive cyclic voltammograms with varying concentrations between 0.50 mmol L⁻¹ and 50 mmol L⁻¹ of lactic acid in degassed 0.50 mol L⁻¹ H₂SO₄ solution at 50 mV s⁻¹, using a Pt modified BDD electrode; inset: zoom view (a). Plot of anodic peak current versus lactic acid concentration (b).

Figure 4b shows the relationship between anodic peak current (I_{pa}) and lactic acid concentration. The experiment was repeated three times at each concentration to evaluate the repeatability and to obtain a standard deviation, indicated by the error bars. It can be seen that I_{pa} increases approximately linearly with lactic acid concentration. The sensitivity of Pt-BDD for lactic acid oxidation is compared to a platinum macro electrode in further section.

3.3. Electro-oxidation of lactic acid at platinum macro electrode

The electrochemical behaviour of a platinum bulk electrode was next investigated in order to compare to the electrochemical activity to Pt-BDD. Cyclic voltammetry was performed at a platinum macro electrode between -0.30 and +1.65 V (vs SCE) in degassed 0.50 mol L⁻¹ H₂SO₄, at 50 mV s⁻¹ (not show). Voltammetric behaviour of platinum macro electrode in degassed 0.50 mol L⁻¹ H₂SO₄ was comparable to Pt-BDD, which ensures that the electroactivity of these electrodes can be compared in this study, as presented in the next section.

Next, with the purpose of investigating the activity of the lactic acid oxidation at platinum bulk electrode, successive lactic acid additions were carried out in degassed 0.50 mol L⁻¹ H₂SO₄ solution. The electrochemical behaviour of this electrode in 0.50 mmol L⁻¹ to 50 mol L⁻¹ of lactic acid is summarised in Figure 5a. The voltammogram of the platinum macro electrode shows an increase of anodic current at *ca.* +1.35 V (vs SCE) and absence of corresponding reduction process, which is similar to the behaviour of Pt-BDD. Next, the dependency of the I_{pa} on lactic acid concentration was verified (Figure 5b). The study of influence of lactic acid concentration was repeated three times at each concentration to evaluate the repeatability and to obtain a standard deviation, indicated by the error bars. It can be seen that I_{pa} also increases monotonically with lactic acid concentration.

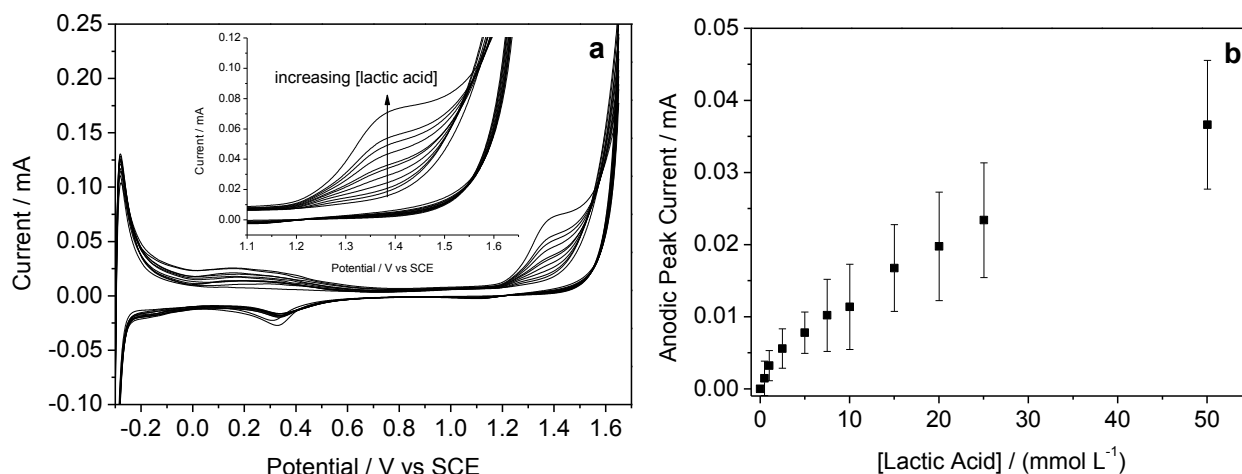


Figure 5. Overlay of successive cyclic voltammograms with varying concentrations between 0.50 mmol L⁻¹ and 50 mmol L⁻¹ of lactic acid in degassed 0.50 mol L⁻¹ H₂SO₄ solution at 50 mV s⁻¹, using Pt macro electrode; inset: zoom view (a). Plot of anodic peak current versus lactic acid concentration (b).

In order to further understand the lactic acid oxidation process on platinum, the transfer coefficient (β)[48, 49] for the mediated oxidation reaction of lactic acid was calculated from a Tafel plot ($\log|I|$ vs potential), at 50 mV s^{-1} in presence of 0.02 mol L^{-1} lactic acid, to be 0.19. This value of β was used in conjunction with Randles-Ševčík equation for an electrochemically irreversible system[50] to estimate the peak current that would be seen for a diffusion controlled process using the diffusion coefficient of lactic acid reported in the literature, $8.59 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. [51] The estimated value was considerably higher than that observed experimentally, suggesting the process is limited by rate of lactic acid oxidation on the platinum surface and not by the lactic acid diffusion.[40-42]

3.4. Comparison between Pt-BDD and Pt macro electrode towards lactic acid oxidation

Next, a comparison of lactic acid oxidation activity is made at the two electrodes (Figure 6a). The figure shows that the peak current at the Pt-BDD is similar in comparison to the platinum macro electrode across the whole concentration range of lactic acid study. However, in order to eliminate the effect of surface area and the comparison to be possible, the raw current response at each concentration of lactic acid is normalised to the electrochemical active area (EAA) at each respective electrode since the lactic acid oxidation is a surface process which takes place likely, on Pt(111) plane.[41, 42] Therefore, the charge involved in hydrogen desorption (Q_H) under the anodic peak at *ca.* -0.26 V (vs SCE) can be utilised to calculate the EAA of platinum microparticles on BDD surface, through Equation 2:[52]

$$\text{EAA} = \frac{Q_H}{220 \mu\text{C cm}^{-2}} \quad (2)$$

where, $220 \mu\text{C cm}^{-2}$ is the charge required to oxidise a monolayer of H_2 on Pt (111).[52] The EAA of Pt-BDD and of platinum macro electrodes are calculated to be 0.74 cm^2 and 0.074 cm^2 respectively. Then peak currents were divided by the EAA of each respective electrode. Figure 6b shows the plot of peak current density for Pt-BDD and platinum macro electrodes against lactic acid concentration.

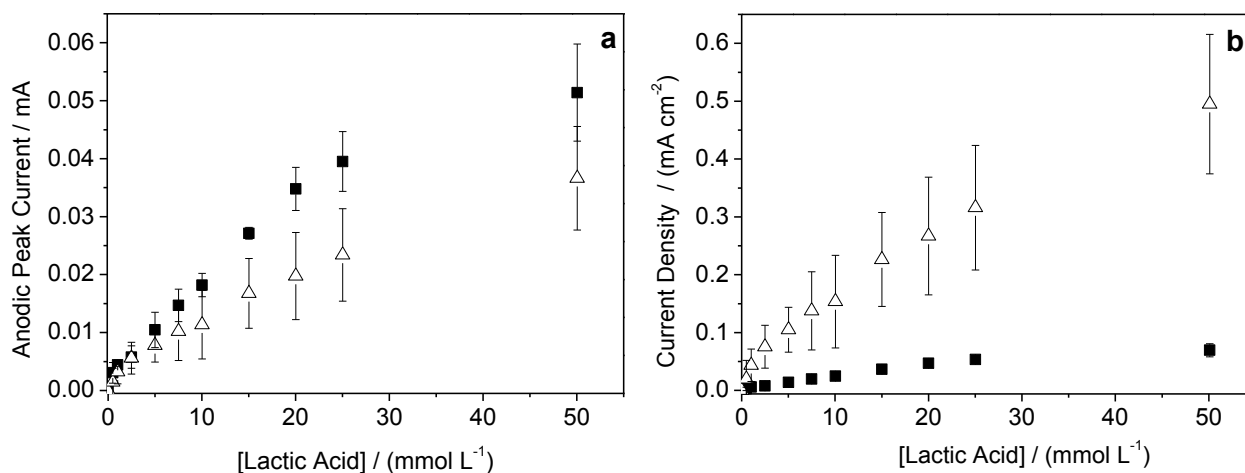


Figure 6. Plot of anodic peak current (a) and anodic peak current density (b) versus lactic acid concentration, for Pt modified BDD (▪) and Pt macro electrode (Δ).

It can be seen that the gradient at platinum macro electrode is around five times higher than Pt-BDD. The conclusion is that there is likely a significant morphology change between bulk and electrodeposited platinum, leading to a markedly change in reactivity with the particulate platinum showing a smaller signal.

4. CONCLUSIONS

In this study, BDD electrode was successfully modified by electrodeposition of platinum microparticles, which showed a mean size of $193 \text{ nm} \pm 107 \text{ nm}$ (SEM) and *ca.* 20 % of platinum coverage (EDX). The performance of the Pt-BDD was compared to a platinum macro electrode via the surface sensitive lactic acid oxidation reaction. A higher reactivity toward lactic acid oxidation was observed at a platinum macro electrode in comparison with a Pt-BDD. This is likely due to morphology changes between the bulk platinum electrode and Pt-BDD. It may be concluded that the replacement of bulk platinum with particulate platinum needs to be viewed with caution in the case of surface sensitive reactions.

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