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Can the mechanical activation (polishing) of screen-printed electrodes enhance their electroanalytical response?†

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The mechanical activation (polishing) of screen-printed electrodes (SPEs) is explored and shown to exhibit an improved voltammetric response (in specific cases) when polished with either commonly available alumina slurry or diamond spray. Proof-of-concept is demonstrated for the electrochemical sensing of nitrite where an increase in the voltammetric current is found using both polishing protocols, exhibiting an improved limit of detection (3σ) and a two-fold increase in the electroanalytical sensitivity compared to the respective un-polished counterpart. It is found that mechanical activation/polishing increases the C/O ratio which significantly affects inner-sphere electrochemical probes only (whereas outer-sphere systems remain unaffected). Mechanical activation/polishing has the potential to be a simple pre-treatment technique that can be extended and routinely applied towards other analytes for an observable improvement in the electroanalytical response.

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Introduction

Recent years have seen the field of analytical electrochemistry emerge as a powerful tool for the analytical chemist, performing rapid *in situ* analyses with a high level of accuracy, sensitivity and selectivity and being comparable to conventional analytical techniques whilst also maintaining a low cost and the ability to be scaled into an ‘in-the-field’ sensor.^{1,2} In light of this, the field of screen-printed electrodes is ever emerging; various carbon forms (particularly graphite), gold and any other working electrode materials can be printed onto inexpensive substrates and, due to their scales of economy, produce cost-effective electrochemical sensing platforms.^{1,3–16} For example, graphite screen-printed sensors have been applied to the detection of a diverse array of analytes; such as novel psychoactive substances,^{17,18} Rohpy-nol®,¹⁹ pindolol,²⁰ atropine,²¹ clonazepam in serum and in

wine,²² nimodipine in pharmaceutical formulations²³ and chemical markers indicative of both cystic fibrosis²⁴ and tuberculosis²⁵ for potential use in breath sensing, as well as many other analytes of both clinical and environmental interest.^{26–36} Screen-printed sensors are often modified to improve their electrochemical response with the addition of various metal compounds,^{37,38} nanoparticles^{39–41} and even organic substrates,⁴² however the implementation of mechanical activation/electrode polishing as a pre-treatment has not been reported contrary to their conventional solid electrode counterparts. In fact, only one proof-of-concept study has been reported by Pravda *et al.*⁴³ who polished a screen-printed electrode (SPE) gently using soft office paper and aggressively using emery paper to improve immunoglobulin (IgG) adsorption. This demonstrated polishing an SPE is plausible, yet the technique has not (to-date), been explored as a pre-treatment to potentially improve their electroanalytical response.

To this end, the following work explores the effect of mechanically activating/polishing SPEs using either commonly utilised alumina slurry or diamond spray and explores what affect this potentially has on their electrochemical activity. We seek to answer the question: can the mechanical activation (polishing) of SPEs enhance their electroanalytical response? Proof-of-concept is shown by using mechanical activation/polishing as a simple pre-treatment step towards the detection and quantification of nitrite; a common environmental pollutant⁴⁴ which electrochemically reacts through an inner-sphere mechanism, *i.e.* is highly dependent and easily affected by changes to surface features.⁴⁵

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Experimental

All chemicals were of the highest grade available and were used as received (without further purification) from Sigma Aldrich (UK). All solutions were prepared using deionised water of resistivity no less than 18.2 M Ω cm and were vigorously degassed with nitrogen to remove oxygen prior to analysis. Sodium nitrite solutions (1 mmol L⁻¹ in pH 7 phosphate buffer solution (PBS)) were used on the day of preparation. Working solutions of lower concentrations were prepared by the appropriate dilution of the stock solution as mentioned above.

Voltammetric measurements were carried out using a Palm-sens (Palm Instruments BV, The Netherlands) potentiostat/galvanostat and controlled by PSTrace version 4.4. All electrochemical measurements were performed at room temperature. The screen-printed graphite electrodes (SPEs), which have a 3 mm diameter working electrode were fabricated in-house with appropriate stencil designs using a microDEK 1760RS screen-printing machine (DEK, Weymouth, UK). This screen-printed electrode design has been previously reported.^{17,19,26–28,30,33,35,46} For the case of each fabricated electrode, first a carbon ink formulation (Product Code: C2000802P2; Gwent Electronic Materials Ltd, UK), which is utilised for the efficient connection of all three electrodes and as the electrode material for both the working and counter electrodes, was screen-printed onto a polyester (Autostat, 250 micron thickness) flexible film. After curing the screen-printed carbon layer in a fan oven at 60 degrees Celsius for 30 minutes, next a silver/silver chloride reference electrode was included by screen-printing Ag/AgCl paste (Product Code: C2040308P2; Gwent Electronic Materials Ltd, UK) onto the polyester substrates, which was subsequently cured once more in a fan oven at 60 degrees Celsius for 30 minutes. Finally, a dielectric paste (Product Code: D2070423D5; Gwent Electronic Materials Ltd, UK) was then printed onto the polyester substrate to cover the connections and define the active electrode areas, including that of the working electrode (3 mm diameter). After curing at 60 degrees Celsius for 30 minutes the SPEs are ready to be used. The electrodes have been characterised electrochemically in prior publications.^{17,20,28} Prior to mechanical activation/electrode polishing, the Ag/AgCl reference electrode was removed (to avoid contamination of the working electrode) and throughout a conventional three-electrode system was used with a screen-printed graphite electrode (working electrode), a platinum wire (counter electrode) and a Saturated Calomel Electrode, SCE, (reference electrode); consequently, all potentials herein are reported *versus* the SCE. The physical geometric size of the respective SPE working electrodes was determined to correspond to 0.071 cm² using callipers. The values of the heterogeneous electron transfer rate constant, k^0 , were determined utilising the Nicholson⁴⁷ method through the use of the following equation: $\psi = k^0[\pi D n \nu F / (RT)]^{-1/2}$ where ψ is the kinetic parameter, D is the diffusion coefficient, n is the number of electrons involved in the process, F is the Faraday constant, R is the universal gas constant and T is the temperature. The kinetic parameter, ψ , is

tabulated as a function of ΔE_p (peak-to-peak separation) at a set temperature (298 K) for a one-step, one electron process with a transfer coefficient, α , equal to 0.5.^{47–49} The function of ψ (ΔE_p), which fits Nicholson's data, for practical usage (rather than producing a working curve) is given by: $\psi = (-0.6288 + 0.0021X)/(1 - 0.017X)^{48,50}$ where $X = \Delta E_p$ is used to determine ψ as a function of ΔE_p from the experimentally recorded voltammetry; from this, a plot of ψ against $[\pi D n \nu F / (RT)]^{-1/2}$ allows the k^0 to be readily determined.

Scanning electron microscope (SEM) images and surface element analysis were obtained with a JEOL JSM-5600LV model equipped with an energy-dispersive X-ray (EDX) micro-analysis package. Raman Spectroscopy was performed using a Renishaw InVia spectrometer with a confocal microscope ($\times 50$ objective) spectrometer with an argon laser (514.3 nm excitation) at a very low laser power level (0.8 mW) to avoid any heating effects. X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Scientific) was also used. All spectra were collected using Al-K radiation (1486.6 eV), monochromatised by a twin crystal monochromator, yielding a focused X-ray spot with a diameter of 400 μ m, at 3 mA \times 12 kV. The alpha hemispherical analyser was operated in the constant energy mode with survey scan pass energies of 200 eV to measure the whole energy band and 50 eV in a narrow scan to selectively measure the particular elements. Thus, XPS was used to provide the chemical bonding state as well as the elemental composition. Charge compensation was achieved with the system flood gun that provides low energy electrons and low energy argon ions from a single source.

Preparation of mechanically activated/polished screen-printed graphite electrodes (SPEs)

A saturated solution containing alumina slurry was dropped onto precision lapping and polishing cloths (Kemet, UK) and the SPEs were mechanically activated/polished for differing times (0.5, 1.0, 3.0 and 10.0 minutes) manually in a figure of eight formation; this is the same protocol used universally to polish conventional solid electrodes and we did not seek to explore whether the polishing pattern would influence the reproducibility of the performance of the SPE, but rather kept this constant. After polishing, the electrodes were washed, placed in a beaker containing deionised water and placed into an ultrasonic cleaner/bath for 15 minutes. Following this procedure, the electrodes were removed and dried at room temperature. The mechanically activated electrodes were then ready for use. The same technique was applied when using Kemet diamond spray in decreasing size order 5 to 3 μ m.

Results and discussion

Screen-printed graphite electrodes (SPEs) were fabricated as described within the Experimental section with the effect of mechanical activation/polishing upon their electrochemical response explored using the redox probe hexaammineruthenium(III) chloride/0.1 mol L⁻¹ KCl; this probe was chosen since



it is an outer-sphere redox probe, which is insensitive to the C/O ratio groups and is affected only by the electronic structure (*i.e.* edge plane like-sites/defects). As shown in ESI Fig. 1† there appears to be a relative increase in the voltammetric peak current following mechanical activation/polishing in comparison to that of a conventional un-mechanically activated/unpolished electrode, suggesting that the process of mechanical activation/polishing potentially has merit as a pre-treatment step to improve its (analytical) electrochemical response. After a subsequent scan-rate study, the working area of the electrode surface, in each instance of polishing time, was estimated using the Randles–Ševčík equation for a quasi-reversible process (at 298 K):^{51,52}

$$I_p = 2.65 \times 10^5 n^3 A D^{1/2} C \nu^{1/2} \quad (1)$$

where I_p is the peak current, n is the number of electrons transferred in the electrochemical process, A is electrode area, D is the diffusion coefficient ($9.10 \times 10^6 \text{ cm}^2 \text{ s}^{-1}$ for hexaammineruthenium(III) chloride),⁵³ C is the redox probe concentration and ν is the applied voltammetric scan rate. The electroactive working electrode area was calculated for all the applied mechanical activation/polishing times (0.0, 0.5, 1.0, 3.0 and 10.0 minutes) which involved SPEs being mechanically activated/polished, with a plot of average peak current ($N = 3$) versus square-root of scan rate being constructed. From the gradient and use of eqn (1), the electrode area was deduced. The average ($N = 3$) electrode areas (and corresponding standard deviation) were found to be 0.0836 (0.0025) cm^2 , 0.0813 (0.0019) cm^2 , 0.0823 (0.0018) cm^2 , 0.0797 (0.0031) cm^2 , 0.082 (0.0028) cm^2 following mechanical activation/polishing times of 0.0, 0.5, 1.0, 3.0 and 10.0 minutes respectively. The ‘roughness factor’ or ‘real’ electro-active area can be estimated through the use of eqn (2):

$$\% \text{Roughness factor} = (A_{R-S}/A_{\text{Geo}}) \times 100 \quad (2)$$

where A_{R-S} is the electro-active area as calculated through the Randles–Ševčík equation (eqn (1)) and A_{Geo} is the geometric area (see Experimental section; 0.071 cm^2).⁵⁴ The roughness factor for each increment of mechanical activation/polishing time, 0.0, 0.5, 1.0, 3.0 and 10.0 minutes, was calculated to correspond to 117.7%, 114.5%, 115.9%, 112.2%, and 115.4% respectively. It is readily evident that despite the perceived increase in the voltammetric peak height as a result of mechanical activation/polishing (*viz.* ESI Fig. 1†), there is in-fact no significant change in the electro-active surface area of the electrode nor the surface roughness. For clarity, the heterogeneous electrode transfer rate constant (k^0) was estimated, for each time of mechanical activation/polishing, as per the Nicholson method⁴⁷ (see Experimental section; note that each value is a result of an average of 3 separate SPEs) with values determined to correspond to 1.49×10^{-3} ($\pm 4.47 \times 10^{-5}$), 9.60×10^{-4} ($\pm 2.02 \times 10^{-5}$), 8.87×10^{-4} ($\pm 4.08 \times 10^{-5}$), 1.20×10^{-3} ($\pm 3.72 \times 10^{-5}$) and 9.78×10^{-4} ($\pm 2.64 \times 10^{-5}$) cm s^{-1} for polishing times of 0.0, 0.5, 1.0, 3.0 and 10.0 minutes respectively. It is clear that there is a marginal initial drop in the k^0 with polishing, however,

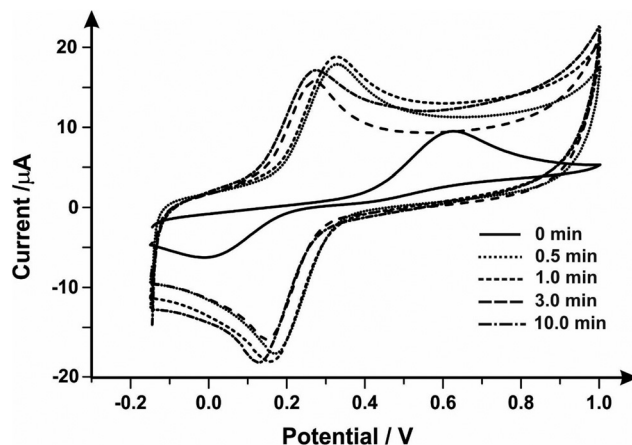


Fig. 1 Cyclic voltammetric responses obtained using a SPE in 1 mmol L^{-1} ammonium iron(II) sulfate/0.2 M HClO_4 solution as a result of varying mechanical activation/polishing times using alumina slurry. Scan rate: 50 mV s^{-1} vs. SCE.

whilst there are minimal further changes, there is no strong correlation (either positive or negative). It can be theorised that mechanical activation/polishing has no effect on the heterogeneous electron transfer rate constant as evaluated using this outer-sphere redox probe.

Next, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple was explored to evaluate the effect of mechanical activation/polishing. This is an inner-sphere probe which is known to be very sensitive to surface and functional groups, especially carbonyl groups.^{55,56} Fig. 1 presents cyclic voltammetric profiles where the unmodified/unpolished SPE exhibits a very large peak-to-peak separation, 510 mV, which significantly improves from mechanical activation/polishing with peak-to-peak separations of 160, 170, 130 and 130 mV for polishing times of 0.5, 1.0, 3.0 and 10.0 minutes respectively. Thus it is clear that the mechanical activation/polishing results in an improvement in the voltammetric response in this case, which is likely a result of the introduction of carbon–oxygen groups (known to improve electron transfer rate kinetics for this case, see above).

X-ray photoelectron spectroscopy (XPS) was next applied to distinguish any surface changes from mechanical activation/polishing; the results of XPS analysis for the SPEs pre-treated with mechanical activation/polishing with alumina (0.5, 1.0, 3.0 and 10.0 minutes) and a control (no mechanical activation/polishing) are reported within Table 1. De-convolution of the spectra reveals the total atomic percentage of carbon (C%) and oxygen (O%) decreases and increases respectively with increasing time of polishing; the percentage of C–O or C=O moieties present on the surface increased from 1.22% following no pre-treatment to 7.28%, 7.37%, 6.03% and 7.12% for increasing increments of polishing time (0.5, 1.0, 3.0 and 10.0 minutes respectively). Note the presence of $\text{AlO}(\text{OH})/\text{Al}_2\text{O}_3$ which is still present even after the post-treatment (see Experimental section). It is evident that the diminishing in the impurity levels upon polishing is likely the responsible parameter for the sudden increase of oxygen ratio in the XPS data. In



the electron transfer kinetics of inner-sphere redox probes only (*i.e.* the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple is improved due to its surface sensitivity (and the possible beneficial introduction of oxygenated species onto the surface), but not the $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ probe which is outer-sphere and affected only by the electronic structure of the electrode).

Attention was next turned to the proof-of-concept electroanalytical sensing of sodium nitrite; this model analyte was chosen to explore the any potential electroanalytical improvements through the use of utilising mechanically activated/polished SPEs. It has been extensively studied using carbon-based electrodes, allowing us to benchmark our (electro) analytical performance. The sensing of nitrite is of importance because of its potential adverse effect on human health;⁵⁷ although previously thought of as an inert metabolite of nitric oxide (NO), recent studies have shown it can be harmful^{57–59} by forming carcinogenic compounds in the digestive system or interfering in the oxygen availability for tissues.⁴⁵ Nitrite is typically used in the food industry as a colorant or preservative,⁶⁰ excessive and inappropriate use of this substance however can potentially cause harm to the population, creating a global need to rapidly and accurately sense nitrite. Fig. 3 shows the cyclic voltammetric response using mechanically activated/polished and un-mechanically activated/un-polished SPEs with increasing mechanical activation/polishing times recorded in $50 \mu\text{mol L}^{-1}$ sodium nitrite/PBS (pH 7.0) where an electroanalytical oxidative peak is visible at approximately +0.84 V (*vs.* SCE). In accordance with the literature, observable in Fig. 3, there is a significant increase in the intensity of the anodic peak current and a slight shift to more positive overpotentials with increasing mechanical activation/polishing time. Qualitative analysis of the cyclic voltammetry reveals the absence of the reverse reaction (reduction), presenting only the

oxidative peak, *i.e.* it is an irreversible process or has a coupled chemical reaction consuming the oxidised species.^{45,64,65} Also visible from the voltammetric responses, is that the application of 3 minutes mechanical activation/polishing time offers an improved oxidative current of similar intensity to 10 minutes, however for convenience 3 minutes was used herein. As a control measure, the electroanalytical sensing of sodium nitrite was performed using a 9.2 mg alumina surface modified SPE which has not been mechanically activated/polished with additions made over the range $10.0\text{--}90.0 \mu\text{mol L}^{-1}$. This data is presented in ESI Fig. 3† where the response is distinct from that presented in Fig. 4, indicating that the alumina itself is not the result of the improved electroanalytical result from mechanical activation/polishing. The surface modification of differing alumina coverages was explored but was found not to result in any improvement nor produce a response as presented above, such as Fig. 4; clearly the improvement in Fig. 3 is due to the mechanical activation/polishing rather than residual surface alumina.

Next, the response of mechanically activated/polished SPEs was explored towards the electroanalytical detection of nitrite through increasing additions of nitrite into pH 7 PBS. Fig. 4 shows the resulting cyclic voltammograms using a mechanically activated/polished SPE (3 minutes) at various concentrations of sodium nitrite, where analysis of the voltammetric peak current (I_p) as a function of nitrite concentration reveals a linear response (see inset of Fig. 4). Fig. 4 (inset) shows the resulting calibration plot which is linear over the range $10.0\text{--}90.0 \mu\text{mol L}^{-1}$ ($I_p (\mu\text{A}) = 0.15 \text{ A L mol}^{-1} (\mu\text{mol L}^{-1}) + 1.96 \mu\text{A}$; $N = 3$; $R^2 = 0.99$; with an average %RSD of 2.56% across all data points). The limit of detection (3σ) was found to correspond to $0.89 \mu\text{mol L}^{-1}$. The limit of detection is comparable to other reported methods for the detection of nitrite in



Fig. 3 Cyclic voltammetric study of the variation of mechanical activation/polishing times recorded in $50 \mu\text{mol L}^{-1}$ sodium nitrite/PBS (pH 7) using SPEs (different SPE per experiment). Inset: a plot of current as a function of mechanical activation/polishing time (with alumina slurry) variation. Scan rate: 50 mV s^{-1} vs. SCE.



Fig. 4 Cyclic voltammograms obtained from additions of sodium nitrite ($10\text{--}90 \mu\text{mol L}^{-1}$) into pH 7 PB using a 3 minute mechanical activation/polished SPE with alumina slurry using the same SPE throughout the experimentation (scan rate: 100 mV s^{-1} vs. SCE); the dotted line represents the blank (no sodium nitrite) response. Inset: analysis of the voltammetric peak heights as a function of concentration.



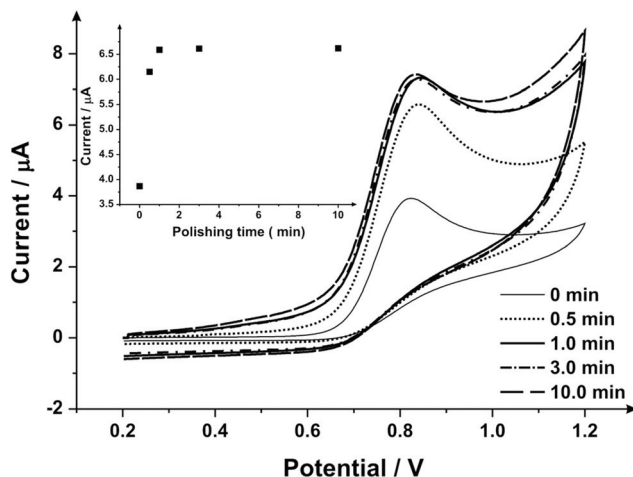


Fig. 5 Cyclic voltammetric study of various mechanical activation/polishing times obtained in 1 mmol L^{-1} sodium nitrite/PBS (pH 7) using SPEs (different SPE per experiment). Inset: a plot of current as a function of the polishing time (with diamond spray) variation. Scan rate: 50 mV s^{-1} vs. SCE.

aqueous media such as: liquid chromatography-amperometric detection of nitrite using a polypyrrole modified glassy carbon electrode doped with tungstodiphosphate anion ($1.00 \text{ } \mu\text{mol L}^{-1}$)⁶¹ and many others in an array of matrices involving complicated, often expensive protocols.^{60,62,63} This is also an improvement over the limit of detection (3σ) determined from the calibration plot obtained following no mechanical activation/no polishing ($I_p (\mu\text{A}) = 0.07 \text{ A L mol}^{-1} (\mu\text{mol L}^{-1}) + 0.33 \text{ } \mu\text{A}$; $N = 3$; $R^2 = 0.99$; with an average %RSD of 4.95% across all data points), revealing a calculated limit of detection (3σ) equal to $2.35 \text{ } \mu\text{mol L}^{-1}$. Also evident from the calibration

curves is that the mechanical activation/polishing pre-treatment offers a greater than two-fold improvement of the electroanalytical sensitivity; $0.15 \text{ A L mol}^{-1}$ following mechanical activation (vs. $0.07 \text{ A L mol}^{-1}$, untreated).

To extend this concept further, SPEs were mechanically activated/polished with diamond spray (which is also commonly used to pre-treat solid reusable electrodes). A cyclic voltammetric study of varying the duration of which the SPEs have been mechanically activated/polished using diamond spray (and using the redox probe hexaammineruthenium(III) chloride/ 0.1 mol L^{-1} KCl) was undertaken – this is shown in ESI Fig. 4.† A similar response as observed earlier (ESI Fig. 1†) is evident, where a relative improvement in electron transfer kinetics is observed (however, in this case no change in the voltammetric peak current is observed). Fig. 5 shows the electrochemical oxidation of sodium nitrite which again shows that mechanical activation/polishing an SPE can result in an increase in the oxidative current; with the voltammetric signal (peak) observed to occur at approximately $+0.80 \text{ V}$ (vs. SCE). Also shown in Fig. 5, in the inset, is the optimum time required to get a satisfactory increase in oxidative current, which is 0.5/1 minutes, as the intensity appears to plateau after this time. These findings are reflected in the SEM micrographs presented in Fig. 6 wherein no apparent improvement in surface ‘smoothness’ is visible after 0.5/1 minutes. EDS analysis (ESI Table 2†), shows a marginal increase in oxygen content from 1.84% to 3.39% after successive polishing times. In light of this, an electrode polished for just 1 minute was selected for further analysis.

The electroanalytical response towards the sensing of sodium nitrite was next explored with additions made into a pH 7 PBS using mechanically activated/polished SPEs with the resulting data presented in Fig. 7 where analysis of the voltam-

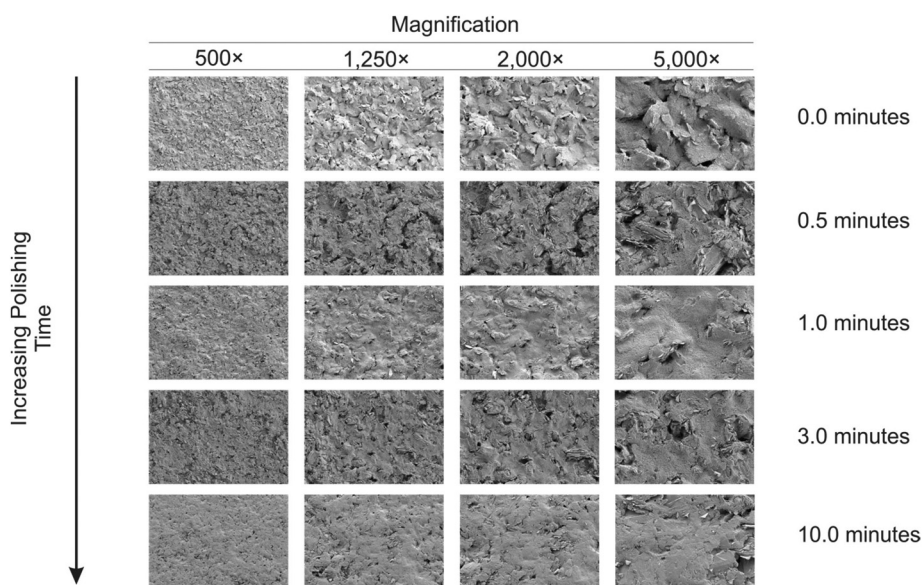


Fig. 6 SEM images of mechanically activated/polished SPEs at four different magnifications for each increment of polishing time using diamond spray.



References

- J. P. Metters, R. O. Kadara and C. E. Banks, *Analyst*, 2011, **136**, 1067–1076.
- J. P. Smith, J. P. Metters, O. I. G. Khreit, O. B. Sutcliffe and C. E. Banks, *Anal. Chem.*, 2014, **86**, 9985–9992.
- K. K. Mistry, K. Layek, A. Mahapatra, C. RoyChaudhuri and H. Saha, *Analyst*, 2014, **139**, 2289–2311.
- M. Li, Y.-T. Li, D.-W. Li and Y.-T. Long, *Anal. Chim. Acta*, 2012, **734**, 31–44.
- M. Arvand, N. Ghodsi and M. A. Zanjanchi, *Biosens. Bioelectron.*, 2016, **77**, 837–844.
- N. Hernandez-Ibanez, L. Garcia-Cruz, V. Montiel, C. W. Foster, C. E. Banks and J. Iniesta, *Biosens. Bioelectron.*, 2016, **77**, 1168–1174.
- P. Kanyong, G. Hughes, R. M. Pemberton, S. K. Jackson and J. P. Hart, *Anal. Lett.*, 2016, **49**, 236–244.
- C. Kokkinos, M. Prodromidis, A. Economou, P. Petrou and S. Kakabakos, *Electrochem. Commun.*, 2015, **60**, 47–51.
- N. Lezi and A. Economou, *Electroanalysis*, 2015, **27**, 2313–2321.
- S. Patris, M. Vandeput, G. M. Kenfack, D. Mertens, B. Dejaegher and J.-M. Kauffmann, *Biosens. Bioelectron.*, 2016, **77**, 457–463.
- A. A. Rabinca, M. Buleandra, A. Balan, I. Stamatin and A. A. Ciucu, *Electroanalysis*, 2015, **27**, 2275–2279.
- K. Senthilkumar, T. N. Sithini, N. Thiyagarajan, S. Baskar and J.-M. Zen, *Electrochem. Commun.*, 2015, **60**, 113–116.
- B. V. M. Silva, B. A. G. Rodriguez, G. F. Sales, M. D. P. T. Sotomayor and R. F. Dutra, *Biosens. Bioelectron.*, 2016, **77**, 978–985.
- P. D. Sinawang, V. Rai, R. E. Ionescu and R. S. Marks, *Biosens. Bioelectron.*, 2016, **77**, 400–408.
- D. Talarico, F. Arduini, A. Constantino, M. Del Carlo, D. Compagnone, D. Moscone and G. Palleschi, *Electrochem. Commun.*, 2015, **60**, 78–82.
- Y. Teng, W. Liu, M. Lan, S. Ma and C. Ma, *Anal. Lett.*, 2016, **49**, 299–306.
- J. P. Smith, J. P. Metters, C. Irving, O. B. Sutcliffe and C. E. Banks, *Analyst*, 2014, **139**, 389–400.
- J. P. Smith, J. P. Metters, O. I. G. Khreit, O. B. Sutcliffe and C. E. Banks, *Anal. Chem.*, 2014, **86**, 9985–9992.
- J. P. Smith, J. P. Metters, D. K. Kampouris, C. Lledo-Fernandez, O. B. Sutcliffe and C. E. Banks, *Analyst*, 2013, **138**, 6185–6191.
- L. R. Cumba, J. P. Smith, D. A. C. Brownson, J. Iniesta, J. P. Metters, D. R. do Carmo and C. E. Banks, *Analyst*, 2015, **140**, 1543–1550.
- O. Ramdani, J. P. Metters, L. C. S. Figueiredo, O. Fatibello and C. E. Banks, *Analyst*, 2013, **138**, 1053–1059.
- K. C. Honeychurch, J. Brooks and J. P. Hart, *Talanta*, 2016, **147**, 510–515.
- P. Salgado-Figueroa, C. Gutierrez and J. A. Squella, *Sens. Actuators, B*, 2015, **220**, 456–462.
- J. P. Metters, D. K. Kampouris and C. E. Banks, *Analyst*, 2014, **139**.
- J. P. Metters, D. K. Kampouris and C. E. Banks, *J. Braz. Chem. Soc.*, 2014, **25**, 1667–1672.
- J. Metters, F. Tan and C. Banks, *J. Solid State Electrochem.*, 2013, **17**, 1553–1562.
- J. P. Metters, R. O. Kadara and C. E. Banks, *Analyst*, 2011, **136**, 1067–1076.
- E. P. Randviir, D. A. C. Brownson, J. P. Metters, R. O. Kadara and C. E. Banks, *Phys. Chem. Chem. Phys.*, 2014, **16**, 4598–4611.
- A. Brotons, L. A. Mas, J. P. Metters, C. E. Banks and J. Iniesta, *Analyst*, 2013, **138**, 5239–5249.
- A. V. Kolliopoulos, J. P. Metters and C. E. Banks, *Anal. Methods*, 2013, **5**, 3490–3496.
- A. V. Kolliopoulos, J. P. Metters and C. E. Banks, *Anal. Methods*, 2013, **5**, 851–856.
- J. P. Metters, S. M. Houssein, D. K. Kampouris and C. E. Banks, *Anal. Methods*, 2013, **5**, 103–110.
- J. P. Metters, R. O. Kadara and C. E. Banks, *Analyst*, 2013, **138**, 2516–2521.
- J. P. Metters, R. O. Kadara and C. E. Banks, *Sens. Actuators, B*, 2012, **169**, 136–143.
- J. P. Metters, F. Tan, R. O. Kadara and C. E. Banks, *Anal. Methods*, 2012, **4**, 3140–3149.
- E. P. Randviir, J. P. Metters, J. Stainton and C. E. Banks, *Analyst*, 2013, **138**, 2970–2981.
- C. W. Foster, J. Pillay, J. P. Metters and C. E. Banks, *Sensors*, 2014, **14**, 21905–21922.
- M. Khairy, R. O. Kadara, D. K. Kampouris and C. E. Banks, *Anal. Methods*, 2010, **2**, 645–649.
- E. Bernalte, C. Marín Sánchez and E. Pinilla Gil, *Sens. Actuators, B*, 2012, **161**, 669–674.
- M. Khairy, D. K. Kampouris, R. O. Kadara and C. E. Banks, *Electroanalysis*, 2010, **22**, 2496–2501.
- C. M. Welch, C. E. Banks, A. O. Simm and R. G. Compton, *Anal. Bioanal. Chem.*, 2005, **382**, 12–21.
- K. C. Honeychurch, J. P. Hart, D. C. Cowell and D. W. M. Arrigan, *Sens. Actuators, B*, 2001, **77**, 642–652.
- M. Pravda, C. O'Meara and G. G. Guilbault, *Talanta*, 2001, **54**, 887–892.
- W. J. R. Santos, P. R. Lima, A. A. Tanaka, S. M. C. N. Tanaka and L. T. Kubota, *Food Chem.*, 2009, **113**, 1206–1211.
- Y. Wang, E. Laborda and R. G. Compton, *J. Electroanal. Chem.*, 2012, **670**, 56–61.
- D. A. C. Brownson, A. C. Lacombe, M. Gomez-Mingot and C. E. Banks, *RSC Adv.*, 2012, **2**, 665–668.
- R. S. Nicholson, *Anal. Chem.*, 1965, **37**, 1351–1355.
- D. A. C. Brownson, S. A. Varey, F. Hussain, S. J. Haigh and C. E. Banks, *Nanoscale*, 2014, **6**, 1607–1621.
- D. A. C. Brownson, D. K. Kampouris and C. E. Banks, *Chem. Soc. Rev.*, 2012, **41**, 6944–6976.
- I. Lavagnini, R. Antiochia and F. Magno, *Electroanalysis*, 2004, **16**, 505–506.
- D. A. C. Brownson, C. W. Foster and C. E. Banks, *Analyst*, 2012, **137**, 1815–1823.



- 52 C. E. Banks and R. G. Compton, *Understanding Voltammetry*, Imperial College Press, 2008.
- 53 L. C. S. Figueiredo-Filho, D. A. C. Brownson, O. Fatibello-Filho and C. E. Banks, *Electroanalysis*, 2014, **26**, 93–102.
- 54 R. O. Kadara, N. Jenkinson and C. E. Banks, *Sens. Actuators, B*, 2009, **138**, 556–562.
- 55 P. Chen and R. L. McCreery, *Anal. Chem.*, 1996, **68**, 3958.
- 56 M. R. Kagan and R. L. McCreery, *Langmuir*, 1995, **11**, 4041.
- 57 J. Lerfall, in *Processing and Impact on Active Components in Food*, ed. V. Preedy, Academic Press, San Diego, 2015, pp. 433–438, DOI: 10.1016/B978-0-12-404699-3.00052-4.
- 58 M. Abdollahi and M. R. Khaksar, in *Encyclopedia of Toxicology*, ed. P. Wexler, Academic Press, Oxford, 3rd edn, 2014, pp. 334–337, DOI: 10.1016/B978-0-12-386454-3.01206-9.
- 59 N. S. Bryan, *Free Radicals Biol. Med.*, 2006, **41**, 691–701.
- 60 D. Zhang, Y. Fang, Z. Miao, M. Ma, X. Du, S. Takahashi, J.-i. Anzai and Q. Chen, *Electrochim. Acta*, 2013, **107**, 656–663.
- 61 Z. Liu, X. Xi, S. Dong and E. Wang, *Anal. Chim. Acta*, 1997, **345**, 147–153.
- 62 X.-H. Pham, C. A. Li, K. N. Han, B.-C. Huynh-Nguyen, T.-H. Le, E. Ko, J. H. Kim and G. H. Seong, *Sens. Actuators, B*, 2014, **193**, 815–822.
- 63 L. Zhou, J.-P. Wang, L. Gai, D.-J. Li and Y.-B. Li, *Sens. Actuators, B*, 2013, **181**, 65–70.
- 64 Q. Li, C. Batchelor-McAuley and R. G. Compton, *J. Phys. Chem. B*, 2010, **114**, 7423–7428.
- 65 R. G. Greenler, *J. Chem. Phys.*, 1962, **37**, 2094–2100.
- 66 D. A. C. Brownson, P. J. Kelly and C. E. Banks, *RSC Adv.*, 2015, **5**, 37281–37286.

