

A facile electrochemical intercalation and microwave assisted exfoliation methodology applied to screen-printed electrochemical-based sensing platforms to impart improved electroanalytical outputs

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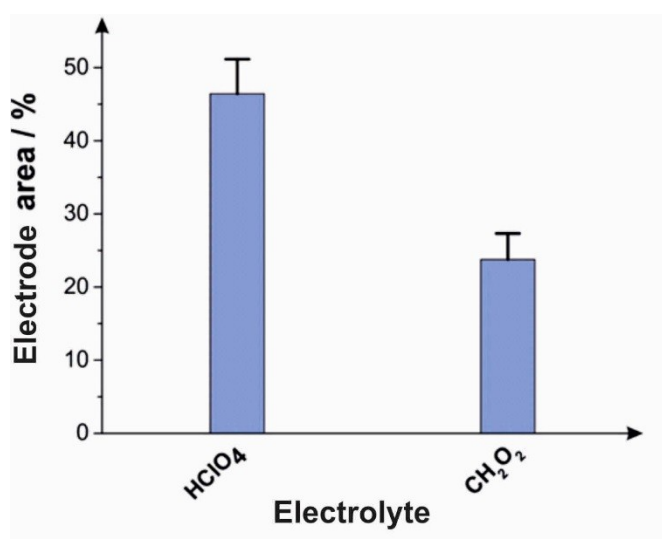
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Electronic Supporting Information (ESI)

Optimisation of the intercalation step (step i):

ESI Fig. 1 demonstrates the increase in the electrode area (%) obtained when utilising the two supporting electrolytes (independently). The conditions employed to form the intercalation products are: an applied anodic potential of +1.2 V (vs. Ag/AgCl) for 300 seconds within 0.1 M HClO₄ and 0.1 M CH₂O₂. The expansion step is performed by microwave heating at 231 W for 60 seconds. It is clear from inspection of ESI Fig 1 that HClO₄ provides a major expansion of the electrode area, double that of CH₂O₂.

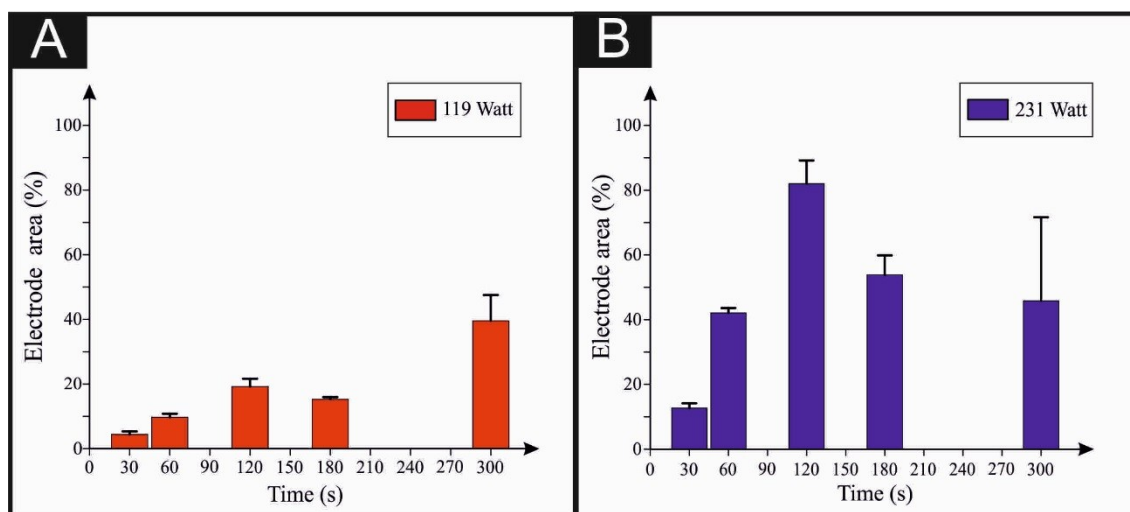


ESI Figure 1. Increases of the electrode area/ effective electrode area with different supporting electrolytes. The electrode area is deduced electrochemically (see Electrochemical Characterisation section) using a redox outer-sphere probe.

Optimisation of the expansion step (step ii)

Two different heating sources, microwave irradiation (231 W, 60 seconds) and a fan oven (120 °C for 3 hrs) were explored in order to deduce which provide the most beneficial output. Note that experimentally the electrode is placed into a beaker of de-ionised water and placed within the microwave. In comparison of the two heating sources, we did not see any improvement in the electrode area, which is likely due to the temperature of the fan oven not being high enough for the removal of the intercalated electrolyte. Hence, for speed and productivity, we chose the microwave irradiation as the heating/expansion step.

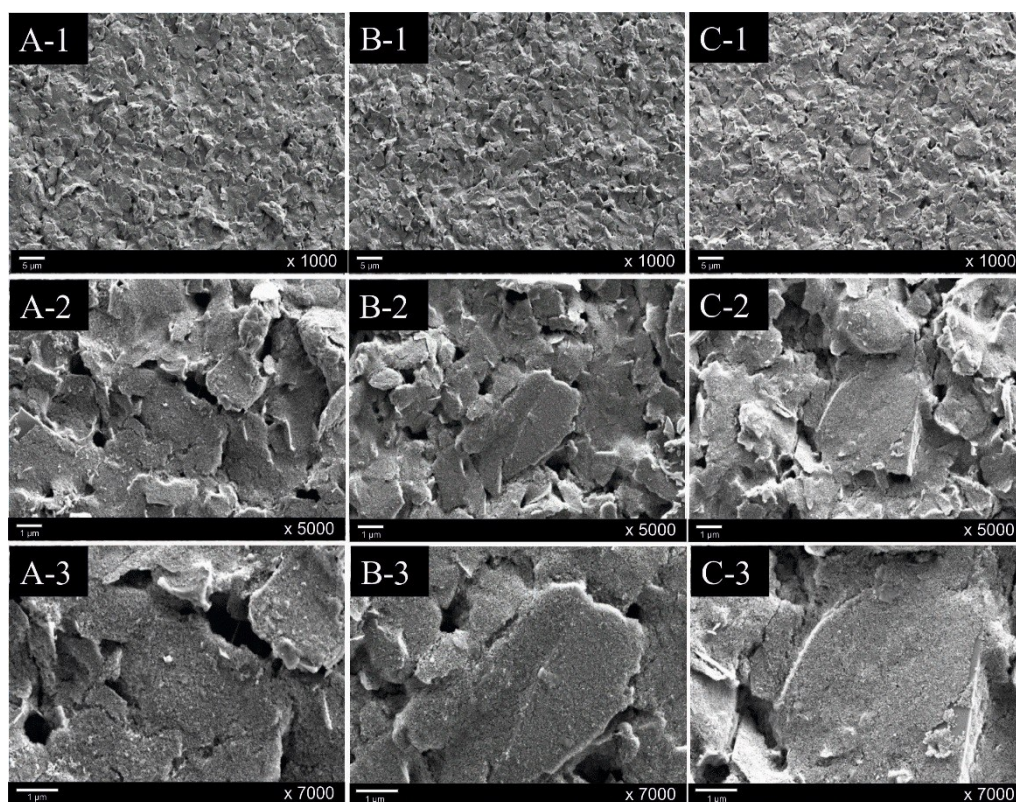
ESI Fig. 2 A and B demonstrate the effect of different microwave irradiation times for two different powers (119 and 231 W), where it is clear the largest increase of the electroactive area occurs at a microwave irradiation power and time of 231 W and 120 seconds respectively. It is important to note, that at times greater than 180 seconds at 231 W, the temperature of the de-ionised water reaches boiling and causes the printed layer to peel off the supporting substrate.



ESI Figure 2. The effect of the microwave irradiation power and time upon the electrode area of the SPEs for 119 W (A) and 231 W (B) utilising HClO_4 as the electrolyte.

Physicochemical Characterisation

ESI Fig. 2 depicts scanning electron microscopy (SEM) imaging of the SPEs (A1-3) and EDI-SPEs (C1-3) following the EDI (B1-3) and both the intercalation/microwave expansion step (C1-3). From the inspection of the SEMs, the applied intercalation and expansions steps appear, at first sight to not significantly alter the surface morphology of the SPE. We conclude that the SEM resolution is not sufficient to see the observed improvement in the electrochemical area as identified above, however these small surface orientated changes are more noticeable within the electrochemical experiments carried out herein.



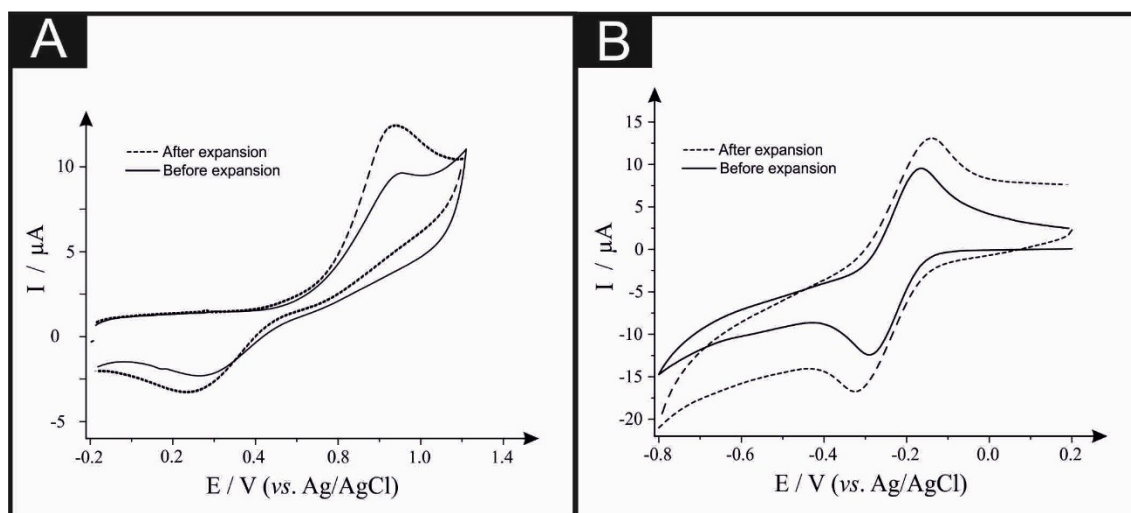
ESI Figure 3. Scanning electron microscopic (SEM) images of unmodified SPEs A), intercalated-SPEs B), and EDI-SPEs C) at different magnifications (1: 1.00 K X, 2: 5.00 K X, 3: 10.00 K X).

Electrochemical Characterisation of the EDI-SPE

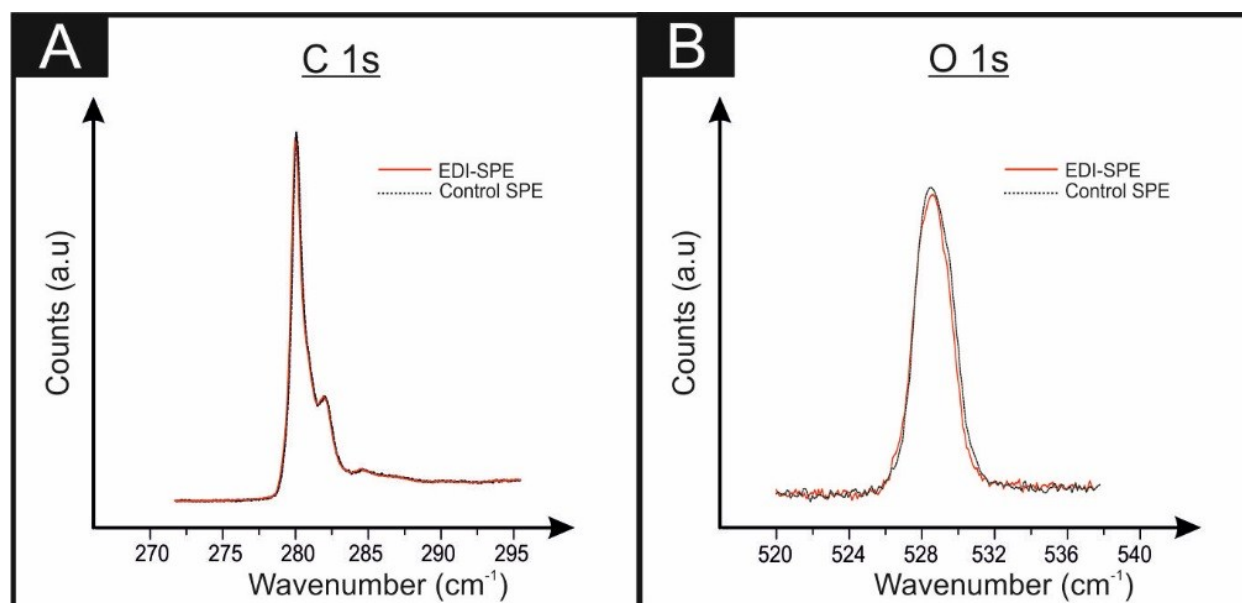
The electrochemical characterisation of the EDI-SPEs (modified under the optimum conditions of 120 s and 231 W) were performed utilising the inner-sphere probe, ammonium iron(II) sulfate, which is known to be sensitive to oxygenated surface and functional groups, such as carbonyl and hydroxyl groups.³ ESI Fig. 4 presents cyclic voltammetric profiles (of an unmodified and an EDI-SPE) where it is clear that both SPEs exhibit a large peak-to-peak separation (~ 500 mV), clarifying that both the intercalation and expansion steps do not induce any significant oxygenated species upon the electrode surface.³⁻⁵

Next, the electrochemical characterisation of the EDI-SPEs using the redox probe hexaammineruthenium (III) chloride was next undertaken. The utilisation of this probe has been chosen due to its outer-sphere redox mechanism that is only affected by the electronic structure of the graphite (*i.e.* edge plane like-sites/defects).⁶ Presented within

ESI Fig. 4 are cyclic voltammograms of the modified and unmodified SPEs, where the former demonstrates a larger capacitance and peak current over the latter, with a slight increase within the peak potential. To corroborate this we have also calculated the standard heterogeneous rate constant, k^0 . The values obtained are $1.72 \times 10^{-3} (\pm 1.23 \times 10^{-4})$ cm s^{-1} and $1.25 \times 10^{-3} (\pm 1.05 \times 10^{-4})$ cm s^{-1} for the SPEs and the EDI-SPE respectively ($N=3$) it is clear that in this case, the modification process has no significant electronic change, as evaluated using the k^0 .



ESI Figure 4. Cyclic voltammetric responses recorded in ammonium iron (II) sulfate / 0.2M HClO₄ (A) and 1mM hexaammineruthenium(III) chloride / 0.1 M KCl (B) utilising unmodified SPEs (solid line) and EDI-SPEs (dotted line). Scan rate: 0.05 V s^{-1} .



ESI Figure 5. XPS analysis of the unmodified SPEs and EDI-SPEs.

References

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