Screen-printable silver nanoparticulate-based inks for the electrocatalysis of hydrogen peroxide

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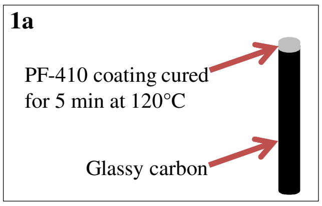
The detection of hydrogen peroxide has been shown to be very important in recent years due to its relevant role in many industrial applications as well as biological reactions. We are interested in it as a quantitative marker for oxidase-based biosensor applications where it is produced when substrate (e.g., glucose, cholesterol) is catalysed by its respective oxidase enzyme.

Previously, a commercial silver flake-based screen-printing ink (PF-410, Acheson®), when treated with surfactant and salt (dodecylbenzenesulfonic acid (DBSA) and KCl) has shown to significantly enhance the electrochemical reduction of hydrogen peroxide up to 80-fold over non-treated inks. In this study, the silver morphology, size and silver supplier is investigated for its effect on the electrocatalysis of hydrogen peroxide. In order to do this, inks loaded with silver micron-sized flakes and silver nanopowders, from various suppliers, are prepared using the binder material extracted from the Acheson® PF-410 to formulate inks.

H_2O_2 Sensor Fabrication

The study of the effect of silver source, morphology and particle size was done by using a binder/carrier system from the commercial Acheson® PF-410 ink. This binder/carrier solution was obtained by a simple centrifugation of the commercial PF-410 ink to remove the silver. This binder solution was then blended with the different types of silver materials (75% w/w) and their electrocatalysis of H_2O_2 was studied by dip coating the various silver conductive inks on GC electrodes which were then analysed by using amperometry (-0.1 V vs Ag/AgCl in PBS pH 7.4). A surfactant/salt solution was used to modify the electrodes by dipping the GC electrodes into a solution of 3.3×10^{-2} M DBSA/0.1 M KCl for at least 30 min before electrocatalysis.

Electrocatalysis using PF-410 Silver Ink



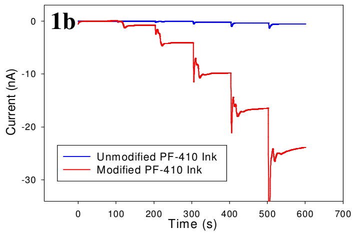
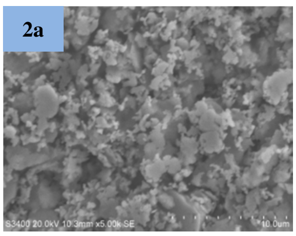


Fig. 1a is a schematic of glassy carbon dip-coated with silver ink (75% w/w silver). Fig.1b Amperometric responses showing a 35-fold increase in current as a result of the PF-410 coating modification with DBSA/KCl on sequential additions of 1 mM H_2O_2.

PF-410 ink (Fig. 2a) shows a typical surface of a PF-410 ink coating which appears to contain silver flakes of varying sizes. The DBSA/KCl modified PF-410 surface (Fig. 2b) shows no evident change in morphology despite exhibiting a 35-fold increase in catalytic current upon H_2O_2 catalysis. This may indicate that the modification process may not be a result of a physical change in morphology, after exposure to DBSA/KCl.



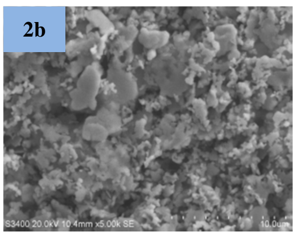


Fig. 2. SEM images of (a) unmodified PF-410 ink and (b) DBSA/KCl modified PF-410 ink modified for 30 min. Accelerating voltage 20 kV. (5.0 k × magnification).

Effect of DBSA/KCl Modification

Depending on the commercial source of the silver flakes, there are varying degrees of electrocatalysis of H_2O_2 (Table 1). The Acheson® PF-410 ink performed least well while the Inframat® micron-sized flakes performed best. However upon modification of the coatings with DBSA/KCl, the Acheson® PF-410 ink shows the greatest increase in catalysis of H_2O_2.

Table 1: Effect of modification on different silver suppliers.

Supplier	Acheson®	Sigma Aldrich®	Inframat®
Ag Particle Size Range	Unknown	10 µm	5-7 µm
Current for 5 mM H_2O_2 @ bare electrode (nA)	0.8 ± 0.3	16 ± 10	184 ± 44
Current for 5 mM H_2O_2 @ modified electrode(nA)	28 ± 9	125 ± 6	190 ± 35
Fold increase upon modification	≈ 35.0	≈ 7.8	≈ 1.0

Effect of Silver Particle Size on H_2O_2 Catalysis

Preliminary silver size study results (Table 2) indicate that the varying sizes of the silvers used has no effect on the catalytic behaviour of the coating. Because of the large standard deviations in this study, it is difficult to ascertain whether or not there is a significant difference in electrocatalysis by the different sized silver flakes.

Table 2: The effect of silver size on the catalysis of H_2O_2.

Inframat® Ag particle size range	5-7 µm	100-500 nm	60 nm
Current for 5 mM H_2O_2 @ bare electrode (nA)	184 ± 44	87 ± 50	171 ± 94
Current for 5 mM H_2O_2 @ modified electrode(nA)	190 ± 35	113 ± 32	187 ± 87
Fold increase upon modification	≈ 1.0	≈ 1.3	≈ 1.1

Conclusion

The source, size and morphology of the silver used has been shown to each have some effect on the catalysis of H_2O_2, however the quality of the silver used has been shown to be more important than the modification of the silver inks. The specific property that is varying across the different silver sources that is contributing to the variation in electrocatalysis. Currently, the factors that may be contributing to the variation in electrocatalysis are being investigated.

Reference

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