

Towards Understanding a Distinct Hydrogen Peroxide Electrochemical Enhancement Using Surfactant-Based Coatings on Silver

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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 coated 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, presence of dispersant and silver supplier is investigated for their effects 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.

H₂O₂ electrocatalytic study

The study of the effect of silver source, morphology and particle size was done by blending various Ag materials with a binder/carrier system from the Acheson® PF-410 ink. This binder/carrier solution was obtained by a simple centrifugation to remove silver. This binder solution was then blended with the different types of silver (75% w/w) and their electrocatalysis of H₂O₂ was studied by dip-coating the various silver conductive inks on glassy carbon (GC) electrodes. Films were cured at 120 °C for 5 min. Analysis was done 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 modified GC electrodes into 3.3×10⁻² M DBSA/0.1 M KCl for at least 30 min before electrocatalysis.

Electrocatalysis on Ag and surfactant/salt modified Ag films

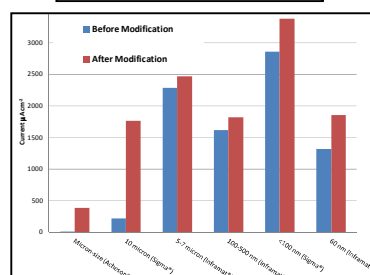
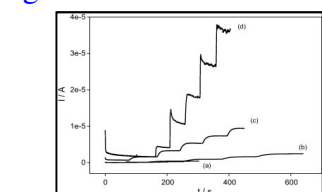
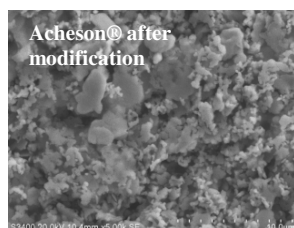
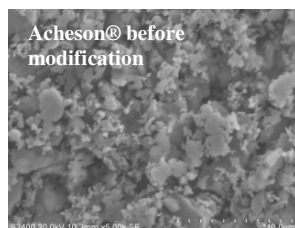
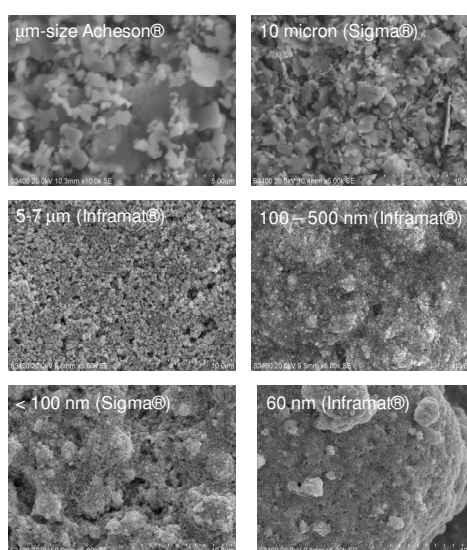


Fig. 1 (left, top¹) Amperometric responses of PF-410 silver paste screen-printed electrodes measured at -0.1 V (vs Ag/AgCl) in PBS (a) unmodified; (b) 3.3 × 10⁻² M DBSA; (c) 0.1 M KCl and (d) 3.3 × 10⁻² M DBSA/0.1 M KCl modified electrodes, with sequential additions of 1 × 10⁻³ M H₂O₂. Fig. 1 (left, bottom) Amperometric responses showing change in current responses for Ag materials as coatings on GC electrodes before and after DBSA/KCl modification (1 mM H₂O₂).



Film comprising Acheson® Ag (left) shows the surface of the cured coating to contain micron-sized silver flakes of varying sizes. The DBSA/KCl modified Acheson® surface (right) shows no obvious change in morphology despite exhibiting a 35-80-fold increase in catalytic current upon H₂O₂ catalysis. This may indicate that the modification process may not be a result of a change in physical morphology, after modification with DBSA/KCl.

Film morphologies comprising Ag particles



SEM images of Ag films showing morphologies relating to their respective particulate sizes and shapes (flakes and spherical particles). No significant differences in contact angles were observed across the different inks (108.5° + 12.8%).

Correlation of Ag dispersant with catalytic behaviour

Ag Material	µm-size (Ach'n®)	10 µm (Sig'®)	5-7 µm (Inf'at®)	100-500 nm (Inf'at®)	<100 nm (Sig'®)	60 nm (Inf'at®)
Film contact angle (non-modified)	110.9	124.4	110.8	97.4	118.8	88.5
No significant trend/difference						
Dispersant	Unknown	Pristine	PVP-like	PVP-like	PVP	PVP-like
Presence of dispersant broadly correlates with increased catalysis on non-modified Ag surface and a reduced enhancement effect upon modification (Fig. 1b)						
Dispersability in water	< 5 min	0 min	< 30 min	≈ 24 hr	≈ 24 hr	< 40 min
Greater dispersability correlates with presence of dispersant						

Conclusion

Different Ag materials with regard to source, size and the presence of a dispersant have different electrocatalytic effects towards hydrogen peroxide, despite being formulated as inks in equivalent manners. The modification of the cured films comprising these materials with DBSA/KCl has also been shown to result in different catalytic effects towards hydrogen peroxide, depending on the starting silver material. It is possible that there may be an effect due to size and/or the presence of a dispersant on the starting Ag material. The study is ongoing.

¹Gonzalez-Macia, L., Smyth, M.R., Morrin, A., Killard, A.J. (2011). *Electrochimica Acta* Vol. 56, Issue 11 4146 - 4153