Enhanced Electrochemical Reduction of Hydrogen Peroxide at Surfactant/Salt Modified Electrodes

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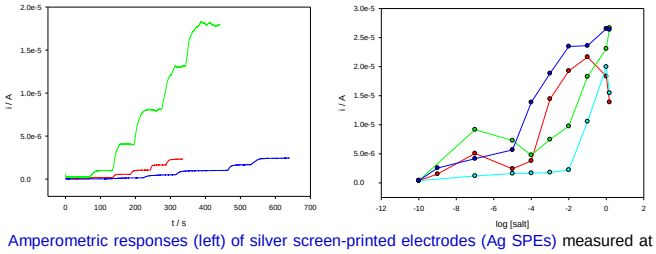
Hydrogen peroxide (H_2O_2) is widely used in many biological systems and industrial processes and its accurate and rapid determination is extremely important. Many metal materials such as Pt, Pd, Cu and Ag have been used as electrodes for the electrochemical determination of H_2O_2. Recently, an improvement of the catalytic activity of silver screen-printed electrodes towards H_2O_2 reduction after electrode modification with a mixed surfactant/salt solution has been reported.

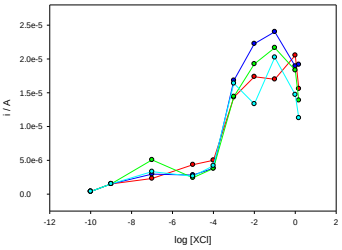
In the present work, this phenomenon is further investigated with regard to the effect the type of metal electrode, surfactant and salt have on the reduction of H_2O_2. Silver paste electrodes were modified with a range of surfactants (DBSA, SDS, CATB, Triton X-100) and chloride salts and their ability to reduce H_2O_2 was evaluated. The effect of the modification on the H_2O_2 reduction was assessed by amperometry. Scanning Electron Microscopy (SEM) measurements were performed to characterize the electrode surfaces before and after the surfactant-based modification. In addition, the surfactant/salt modifications were performed on a range of metallic substrates such as Au, Pt and other Ag-based electrodes. Comparisons of H_2O_2 reduction at these electrodes are shown and the effect of their modifications is also studied.

Effect of surfactant type in the modification solution



Amperometric responses (left) of silver screen-printed electrodes (Ag SPEs) measured at -0.1 V vs. Ag/AgCl: (---) unmodified, (---) SDS modified and (---) SDS/NaCl modified, with sequential additions of 1 mM H_2O_2. Ag SPEs were then exposed to the different surfactant solutions. The plot of the cathodic currents vs log [salt] (right) obtained during amperometric measurements at -0.1 V at 5 mM H_2O_2 showed enhanced catalysis for all the surfactant/salt combinations: (•) DBSA/KCl, (•) Triton X-100/KCl, (•) CTAB/NaBr and (•) SDS/NaCl.

Effect of Group I metal chloride salt in the modification solution

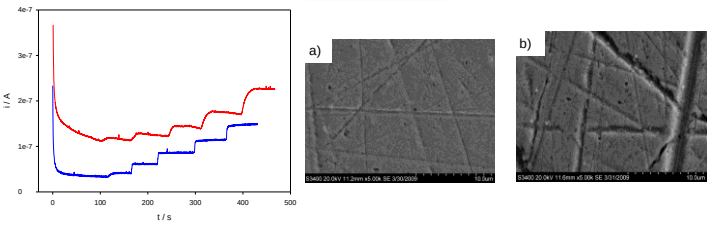


Plot of current vs log [XCl] obtained during amperometric measurements of Ag SPEs at -0.1 V, at 5 mM H_2O_2. Ag SPEs were previously dipped into solutions containing DBSA with a range of concentrations of: (•) LiCl; (•) NaCl; (•) KCl; (•) CsCl. All electrodes showed similar patterns of catalysis with an onset above approx. 10^{-4} M and peaking at 10^{-1} M (except LiCl peaking at 1 M).

The observed enhancement of the electrocatalytic reduction of H_2O_2 on Ag SPE surfaces following surfactant/salt modification has been shown to occur with a range of surfactant and salt combinations including DBSA/KCl, SDS/NaCl, CTAB/NaBr and Triton X-100/KCl. The optimum ratio of surfactant and salt was found to be approximately 3:1 and may relate to the formation of ordered crystalline structures that appear at the electrode surface. It is also suggested that the size of the electrolyte counter-ion affects catalysis by affecting the packing and structural morphology of these structures. The interaction of the surfactant/salt structures with various noble metallic electrode surfaces was also assessed.

Effect of the metallic electrode following surface modification with surfactant/salt

Ag-based electrodes



Amperometric responses of silver (99.9%) metal electrodes (left) at -0.1 V (vs Ag/AgCl): (---) unmodified and (---) DBSA/KCl modified, at H_2O_2 concentrations from 1 to 5 mM. SEM images of the metallic Ag (99.9%) electrodes (right) before and after DBSA/KCl modification. No formation of surface structures as well as enhancement on H_2O_2 reduction was observed following the modification as with Ag SPEs.

Au and Pt-based electrodes

Electrode	Area (cm^2)	j_{unmod} / ($\mu A/cm^2$)	j_{mod} / ($\mu A/cm^2$)	j_{mod}/j_{unmod}
Au SPE AT (Dropsens)	0.126	0.7	8.0	12.2
Au SPE BT (Dropsens)	0.126	0.3	0.5	1.9
Au SPE (DuPont)	0.045 (unmod)/ 0.040 (mod)	1.7	11.2	6.6
Au (99.9%)	0.031	41.1	31.7	0.8
Ag SPE	0.126	3.1	273.6	88.8
Pt SPE (Dropsens)	0.126	481.0	956.3	2.0
Pt SPE (Dupont)	0.035	959.4	910.0	0.9

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