

# Screen-printed platinum electrodes for the detection of cupric and ferric ions in high chloride backgrounds

A. Cranny<sup>1\*</sup>, N.J. Harris<sup>1</sup>, A.P. Lewis<sup>1</sup>, M. Nie<sup>2</sup>, J.A. Wharton<sup>2</sup>, R.J.K. Wood<sup>2</sup> and K.R. Stokes<sup>3</sup>

<sup>1</sup>Electronic Systems and Devices Group, School of Electronics and Computer Science, University of Southampton, Highfield, Southampton, Hampshire, SO17 1BJ, UK

<sup>2</sup>Surface Engineering and Tribology Group, School of Engineering Sciences, University of Southampton, Highfield, Southampton, Hampshire, SO17 1BJ, UK

<sup>3</sup>Physical Sciences Department, Dstl, Porton Down, Salisbury, Wiltshire, SP4 0JQ, UK

\* Corresponding author: Email [awc@ecs.soton.ac.uk](mailto:awc@ecs.soton.ac.uk)

**Abstract:** Screen-printed platinum electrodes developed for use in corrosion monitoring applications have been used to detect cupric and ferric ions both individually and as mixtures in a background of 3.5% by weight sodium chloride and in the presence of dissolved oxygen. In single species detection linear responses for the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  couple were observed over the concentration range 0.3 to 100mM. By contrast, the small size of the working electrode caused a current limiting response for cupric ions over the same concentration range. In mixtures of these ions, the sensors show good differentiation and are able to separate the individual metal ion responses.

**1 Introduction:** Screen-printed platinum electrodes were fabricated using standard thick-film processing techniques. The platinum paste used (Heraeus Silica and Metals, RP10001-145B) is not a conventional thick-film material in that it does not contain a glass binder to hold the functional parts together. Instead, platinum particles are dispersed in an organic resin which is completely burnt away during the firing process. Accordingly, resultant films are of a higher purity and are considerably thinner than normal thick-films with typical thickness less than 1  $\mu\text{m}$ .

The platinum electrodes were printed as 3mm wide strips on 96% alumina substrates (Coors Ceramics, ADS-96R) as shown in Fig. 1. A glass dielectric paste (ElectroScience Laboratories, 4905CH) was then printed over the majority of the platinum electrode length as an insulation layer, leaving one end free as a terminal and a circular window at the other end defining the active electrode area. A final

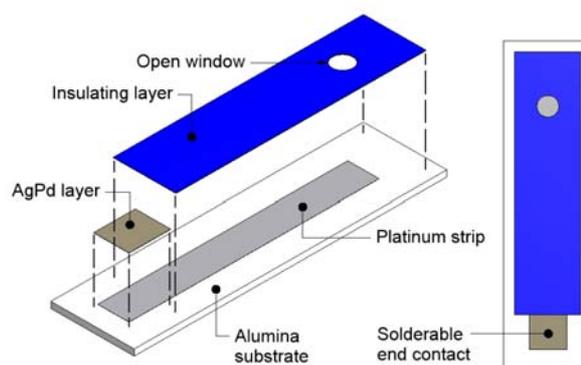


Fig. 1. Schematic of single platinum electrode.

layer of silver-palladium paste (ESL, 9635) was printed over the terminal end to produce a solderable electrical connection.

Stock solutions of cupric and ferric ions were produced by dissolving copper(II) chloride dihydrate (Sigma Aldrich, ACS Reagent, 99+%) and iron(III) chloride hexahydrate (Sigma Aldrich, ACS reagent, 97%) in aqueous solution of 3.5% by weight sodium chloride (VWR, AnalaR, >99.5%). Metal cation concentration levels were varied during experiments by drop-wise addition of aliquots of the stock solutions into a background aqueous solution of 3.5% by weight sodium chloride (~0.6M) using a micropipette. Intentionally, no measures were taken to de-oxygenate the test solutions (in real world measurements we do not always have the ability to de-gas sample solutions). All measurements were performed using an Autolab PGSTAT302N potentiostat (EcoChemie) with potential waveforms set with respect to an Ag/AgCl (3.5M KCl) reference electrode (VWR, GelPlas). Two platinum electrodes were used as the working electrode and counter electrode in standard potentiostatic arrangement with circular areas of diameter 2.0 and 1.5mm, respectively. The analytical technique of

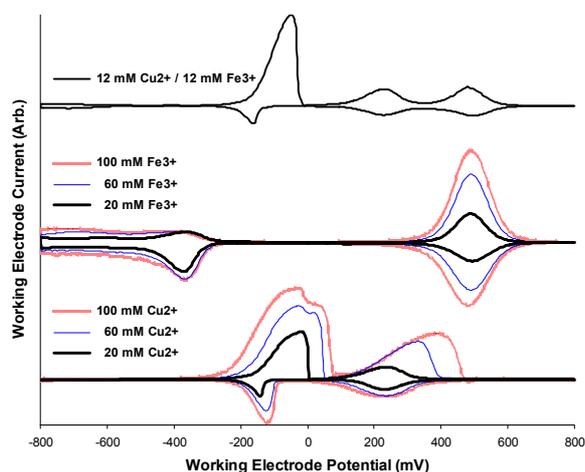


Fig 2. Cyclic voltammograms for cupric ions (bottom), ferric ions (middle) and mixture (top).

cyclic differential pulse voltammetry was chosen to characterise the electrodes. The parameters of the waveform were: potential scan range  $\pm 800$  mV; potential step size  $\pm 5$  mV; interval time 100 ms; pulse amplitude  $\pm 20$  mV and pulse time 40 ms.

**2 Results:** Fig. 2 shows representative voltammograms for cupric ions and ferric ions at three different ion concentrations (20, 60 and 100 mM), as well as for a mixture of ferric and cupric ions at approximately equal concentrations. In the case of the cupric ion response, the two current peaks at the more cathodic potentials represent bulk reduction and oxidation of the cupric ion according to  $\text{Cu}^{2+} + 2e^- \leftrightarrow \text{Cu}$  and demonstrate a shift in peak position with concentration to more anodic potentials in accordance with the Nernst equation. The two current peaks at the more anodic potentials represent monolayer oxidation and reduction of the same ionic reaction (under potential deposition). For the ferric ion response, the current peaks observed at anodic potentials represent the ferric/ferrous redox couple as given by  $\text{Fe}^{3+} + e^- \leftrightarrow \text{Fe}^{2+}$  which occurs at a fixed potential regardless of concentration. The peaks seen at cathodic potentials represent the ferric/iron redox couple as given by  $\text{Fe}^{3+} + 3e^- \leftrightarrow \text{Fe}$ . The top trace in the figure clearly shows that the two metal cations can be individually identified when present in a mixture. It also shows that the response for the  $\text{Fe}^{3+}/\text{Fe}$  couple is absent, implying that once a copper film has plated onto the working

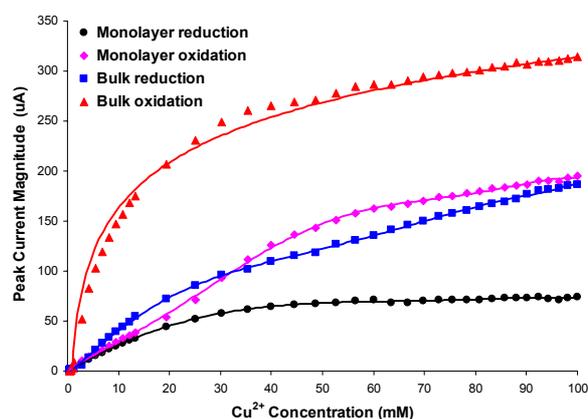


Fig 3. Peak current magnitudes as a function of cupric ion concentration.

electrode surface, the ferric ion can no longer be reduced at this surface.

Calculated values for peak currents as a function of ion concentration are shown in Fig. 3 and Fig. 4 for cupric and ferric ions respectively. Both figures show signs of current limiting with concentration due to the finite size of the working electrode area ( $< 1.8 \text{ mm}^2$ ). The response for the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  couple shows good linear characteristics.

**3 Conclusions:** Screen-printed platinum electrodes are a cheaper, mass-producible alternative to conventional laboratory platinum electrodes. Their ability to detect cupric and ferric ions makes them useful sensors for corrosion measurement applications. Response sensitivity can be improved by increasing the electrode surface area and/or employing more sensitive analytical techniques such as anodic stripping voltammetry.

### Acknowledgements

The authors would like to thank the EPSRC and Dstl for their financial support under EP/F004362/1.

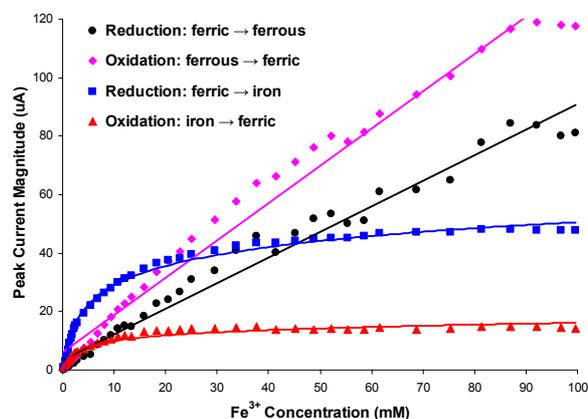


Fig 4. Peak current magnitudes as a function of ferric ion concentration.