DESIGN AND EVALUATION OF NEW OPTICALLY TRANSPARENT THIN-LAYER ELECTROCHEMICAL CELLS

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A new thin-layer spectroelectrochemical cell with an optically transparent thin-layer electrode (OTTLE) has been designed and characterised using ferri/ferrocyanide with potassium chloride supporting electrolyte in aqueous solution as model system. The optical configuration is directed perpendicularly through the OTTLE and solution.

The cell is made of plexiglass and is equipped with two semi-transparent tin oxide coated glass windows at a distance of 50-150μm, i.e. smaller than the semi-infinite electrochemical diffusion layer thickness. The interior volume varies from 1-10μl according to the spacing between the tin oxide windows and can be used either in a stationary mode or in a continuous flow system. Flow cells [1,2] have the advantages of the steady state attainable in a hydrodynamic system, assuming laminar flow within the thin layer cell, and removal of any gaseous reaction products.

Design of the cell is such that platinum wire or tube, or tin oxide coated windows can be used as working or counter electrodes, the reference electrode being Ag|AgCl (0.1M KCl). It can be mounted directly in a conventional spectrophotometer by simply using a small adaptable support.

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All solutions were prepared from triply distilled water and analytical grade reagents.

Cyclic voltammograms of the ferri/ferrocyanide couple in the thin-layer cell, Fig.1, exhibit, at a scan rate of 5mV s^{-1}, some effect from uncompensated resistance due to the cell dimensions.

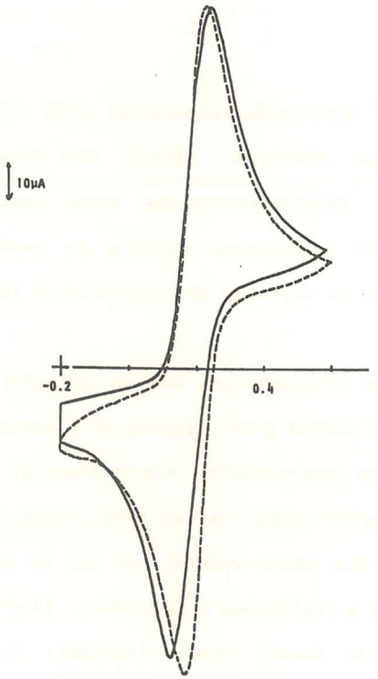

Fig.1 Cyclic voltammograms for 1.4×10^{-3}M $K_4Fe(CN)_6$ in 1.0M KCl in OTTLE cell, thickness 250μm, and scan rate of 5mV s^{-1}. Working electrode SnO_2, reference electrode Ag|AgCl (0.1M KCl) and counter electrode (——) SnO_2 or (---) Pt tube.

The effect of the uncompensated resistance is less when using a much higher concentration of supporting electrolyte, Fig.2, and a very low scan rate of 0.1mV s^{-1}. The difference between the anodic and

cathodic peak potentials in cyclic voltammograms is less than 10mV which suggests a good cell design. The formal potential obtained for the ferri/ferrocyanide system of +0.26V vs. Ag|AgCl (0.1M KCl) is in good agreement with that expected.

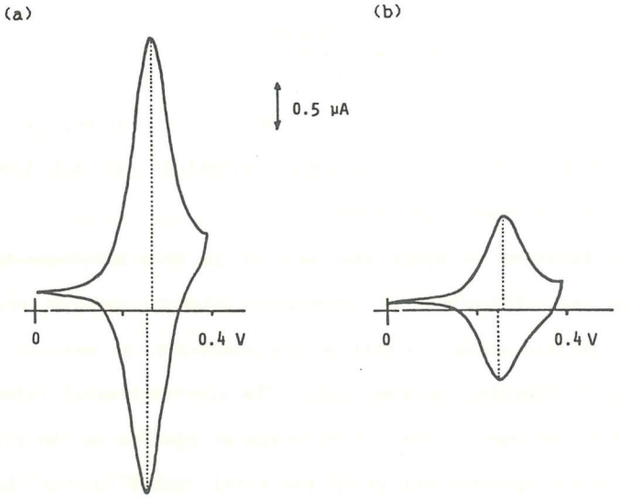

Fig.2 Cyclic voltammograms for 3.9×10^{-4}M $K_4Fe(CN)_6$ in 3.0M KCl in OTTLE cell, thickness 250μm, at a scan rate of 0.1mV s^{-1}. Counter electrode Pt tube, reference electrode Ag|AgCl (0.1M KCl) and working electrode: (a) Pt wire and (b) SnO_2.

Results with this cell in the flow-through mode give the sigmoidal shape obtained in conventional steady-state current-voltage curves.

The voltammograms obtained both in the stationary and flow-through modes show the thin-layer technique is a very long timescale voltammetric technique, as the better results are for scan rates of the order of 0.1mV s^{-1}. However, this could be advantageous for quantitative studies of electrode reactions with small heterogeneous rate constants.

The theory for the electrochemical behaviour of thin-layer cells is well established [3]. The oxidation and reduction peaks are symmetrical about $E^{\circ'}$, the current maximum occurring at E_p, and i_p is directly proportional to scan rate

$$i_p = \frac{n^2F^2VC_R^{\circ}v}{4RT}$$

where v is scan rate, V is the cell's interior volume, C_R° is the initial concentration of R (assuming oxidation) and all the other symbols have the usual significance.

It is intended to apply the cell to *in situ* spectrophotometric monitoring of uv/vis/near-ir absorbance changes due to electrode reactions of biologically electroactive compounds, as well as for the detection of absorbing intermediates. The electrochemical information is a current related to the concentration of species on the electrode surface, while spectroscopy gives the total amount of the absorbing species in the cell. Complementary information from the two techniques should be valuable in elucidation of reaction rates and mechanism.

References

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ELECTROCHEMICAL BEHAVIOUR OF RHODIUM CONTAINING $NiCo_2O_4$ ELECTRODES

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1. INTRODUCTION

The spinel type oxide $NiCo_2O_4$ is one of the most promising anode materials for oxygen evolution in alkaline solution |1|. Haenen *et al.*|2| have studied the $NiCo_2O_4$ electrocatalytic activity as a function of its structural and physico-chemical properties. It has also been shown that the electrocatalytic activity presented by this oxide is determined not only by the surface area and morphology, but also by the surface composition, since the oxygen evolution reaction occurs *via* the formation of surface higher oxides on the reactive sites |3|. These studies have demonstrated the importance of characterizing the oxide electrode surface.

In the present work, two sets of electrodes were prepared: $NiCo_2O_4$ electrodes and $NiCo_2O_4$ electrodes modified by the presence of Rh^{3+} cations. The partial substitution of cobalt by rhodium was motivated by the high stability of this element in the (+3) oxidation state and also by its preference in occupying the octahedral sites in the spinel structure. Moreover, this substitution may lead to a better understanding of the role of cations located in octahedral sites in the corresponding electrode activities.

Preliminary studies made with $NiCo_2O_4$ electrodes, prepared at 300, 350 and 400°C showed that their behaviour is strongly dependent on the temperature of synthesis, T_s |4|. It has also been observed that the activity, as measured by the current density, increases as T_s decreases.