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Preparation of a New Modified Electrode with Copper(II)–Glycylglycine Complex

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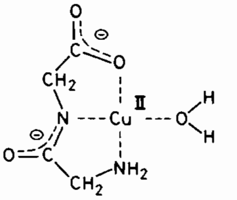
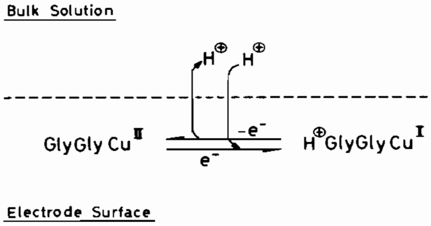
There is considerable interest in the properties of electrodes that have molecular surfaces [1]. Such electrodes may catalyze electron transfers between the electrode and substrate molecules in solution. We report here preparation of a new kind of modified electrode with copper(II)–glycylglycine complex (GlyGlyCu^{II}) [2, 3] on the surface of a glassy carbon electrode. This study is based upon one in which the properties of the GlyGlyCu^{II} complex were investigated as a function of pH [3].



GlyGly Cu^{II}

Cyclic voltammograms for the complex at pH 11.0 at a glassy carbon electrode are shown in Fig. 1. When the potential applied was cycled between +0.3 and −0.5 V *vs.* SCE, no redox waves were seen (Fig. 1a).



Scheme 1.

However, a redox wave appeared after an electrode potential more negative than −0.6 V *vs.* SCE had been applied. The magnitude of the wave, that is, of the cathodic and anodic peak currents, increased with time at the negative potential or with repeated scans, for instance, between +0.3 V and −0.8 V *vs.* SCE. After the potential applied was cycled within this region six times, clear cathodic and anodic peaks appeared (Fig. 1b). This cyclic voltammogram was produced again after the electrode was rinsed thoroughly with water and then immersed in an aqueous solution containing only the supporting electrolyte at the same pH (Fig. 1c). These results show that when the complex in the bulk solution was reduced at the electrode, it became deposited onto it and took on other redox properties (Scheme 1). Peak currents in the cyclic voltammogram decreased to 85% of the original value with enough electrode rinsing, probably because the attached complex was partly washed out; peak potentials and the ratio of cathodic to anodic peak currents did not change. We attributed this cyclic voltammogram to a redox couple of Cu$^{II/I}$ complexes. A second irreversible wave corresponding to the reduction of Cu^{I} complex to Cu^{0} appeared at potentials more negative than −0.7 V *vs.* SCE and was not examined in this study. The reason for a small anodic peak appearing as a shoulder at ±0 V *vs.* SCE (Fig. 1b and c), was not clear, but it may be due to formation of two kinds of Cu^{I} complexes or to variations in the adsorption energy.

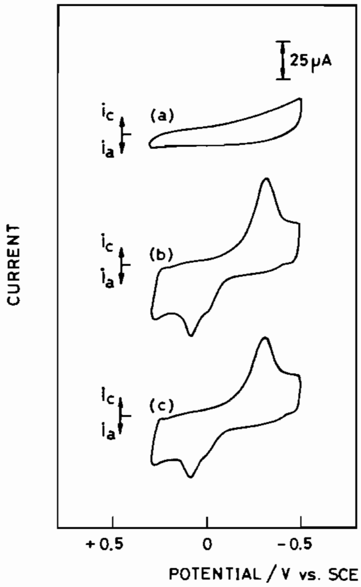


Fig. 1. Cyclic voltammograms of GlyGlyCu^{II} at a glassy carbon electrode at 25 °C. The aqueous solution ([GlyGlyCu^{II}] = 1.0×10^{-3} mol dm^{-3}; [NaClO$_4$] = 1.0×10^{-1} mol dm^{-3}; at pH 11.0 ± 0.2) was purged with pure nitrogen gas. Scan rate: 0.5 V s^{-1}. Measurements: (a) without treatment, (b) after six potential cycles between +0.3 V and −0.8 V *vs.* SCE, and (c) in an aqueous solution containing only the supporting electrolyte at the same pH with the electrode used for (b).

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This system was durable for thousands of repeated scans in the potential region between +0.3 and −0.5 V *vs.* SCE with only a slight decrease in the peak currents, less than 0.05% of their original values in each cycle. The extent of adsorption of the complex onto the electrode was estimated from single-step chronocoulometric measurements in which the potential stepped from +0.3 to −0.5 V *vs.* SCE. The total coulombs of electricity amounted to 31 μC cm^{-2}, which corresponds to an electrode bearing one or a few layers of the complex, of the order of 10^{-10} mol cm^{-2} [4].

The cathodic and the anodic peak potentials depended on the pH of the bulk solution, both shifting to negative potential with increasing pH. These shifts were 56 ± 3 mV/pH unit, which corresponds to one-electron transfer followed by one-proton transfer [5]. Changing the supporting electrolyte from sodium perchlorate to potassium chloride did not alter the cyclic voltammogram. This suggests that charge neutralization of the complex on the electrode with the electron transfer is not accomplished by doping and undoping of the electrolyte, but only by a proton transfer from the bulk solution to the complex and *vice versa.*

At the surface of this electrode, the adsorbed complex was electroactive and its redox coupled with proton transfer. Deprotonated amide nitrogen or carboxylate oxygen of the GlyGly ligand may serve as the proton accepting site.

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