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Salt matrix voltammetry: Microphase redox processes at ammonium chloride | gold | gas triple phase boundaries

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ABSTRACT

Electrochemical processes at the electrode | ammonium chloride salt crystal | gas triple phase boundary are detected under the condition that (i) microscopic contact points of salt crystals to a suitable working electrode are formed and (ii) the relative humidity level is adjusted to allow sufficient surface ion conduction in a thin water film within the salt matrix. In this preliminary report, redox systems such as $Fe(CN)_6^{3-/4-}$, hydroquinone/benzoquinone, decamethylferrocene$^{+/0}$, ferrocenedimethanol$^{+/0}$, and $Cu^{2+/+/0}$ are investigated embedded into an ammonium chloride salt matrix (by mechanical grinding) and then brought into contact with a macroscopic gold disc electrode. Voltammetric current responses are demonstrated consistent with the processes in the microphase formed at the salt | electrode | gas triple phase boundary. Copper metal electro-deposition is observed. Direct electrochemistry of dioxygen from the gas phase at the salt crystal | gold electrode contact is observed and gas sensing applications are proposed.

1. Introduction

Electrochemical processes require a reactive contact between an electron conductor and an ion conductor. By limiting this contact to a microscopic point (or an array of points) problems due to mass transport limitations or due to limited electrical or ion conductivity can be minimised. Prominent examples for the processes at microscopic point contacts are electrochemical reactions at micro- [1] and nano-electrodes [2]. This study focuses on the microscopic point contacts between a crystalline solid and a solid electrode in the presence of a humid gas.

Previous work on the electrochemistry of solid materials has been devoted to processes at solid | solid interfaces [3] and in liquid electrolyte environments [4] with particular emphasis on microparticle deposits [5]. The electrochemical system in the latter case is characterised by a triple phase boundary process, e.g. the solid | liquid electrolyte | solid electrode interface reported for example for chromium carbonyl complexes [6]. The concept of triple phase boundary reactivity has been further exploited in liquid | liquid electrolyte | solid electrode systems where ion transfer from an aqueous electrolyte phase into an oil phase was observed [7,8].

In the present report the triple phase boundary ammonium chloride solid | gold electrode | gas is investigated. Fig. 1 shows a schematic drawing of the electrochemical cell with an ammonium chloride salt situated between a working electrode and a counter/reference electrode. It is demonstrated that redox systems immobilised by mechanical grinding onto the surface of the ammonium chloride salt allow well-defined voltammetric responses to be observed. Implications for electroanalysis and gas sensing are discussed.

2. Experimental details

2.1. Chemical reagents

Analytical grade ammonium chloride, potassium ferrocyanide, ferrocenedimethanol, decamethylferrocene, hydroquinone and copper sulphate were purchased from Sigma-Aldrich (UK) and were used without further purification. Demineralised and filtered water taken from a Thermo Scientific water purification system (Barnstead Nanopure) with 18.2 MΩcm resistivity was used for the preparation of the saturated solution of ammonium chloride. Argon gas (Pureshield, BOC) was used with controlled relative humidity.

2.2. Instrumentation

A two-electrode electrochemical set-up was employed with a 2 mm diameter gold disc electrode (CH Instruments) as the working electrode and a saturated calomel electrode (SCE, Radiometer, Copenhagen) as the reference/counter electrode. The SCE electrode is used here in the reference/counter mode only for low currents where the reference potential remains un-effected. All measurements

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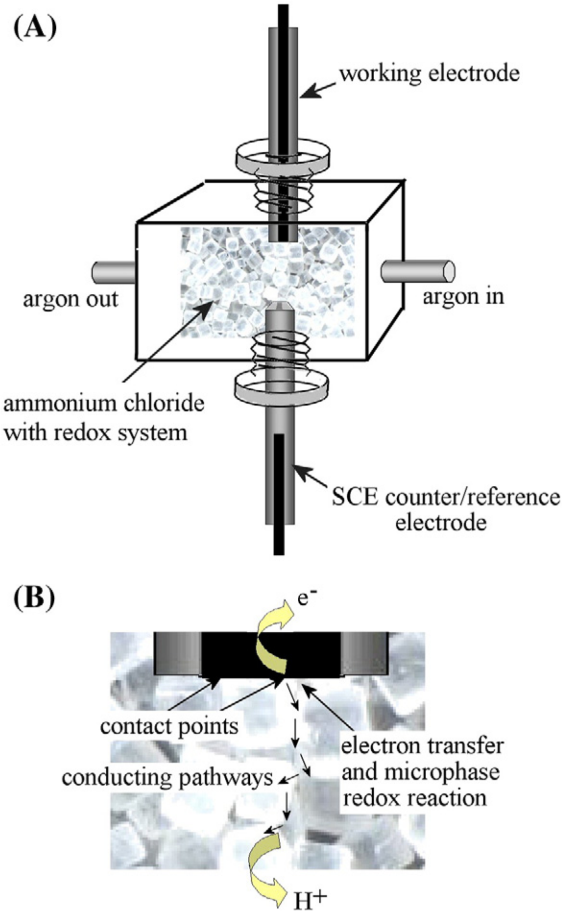

Fig. 1. (A) Schematic drawing of the electrochemical cell with an SCE counter/reference electrode and a gold disc working electrode. A redox system is immobilised onto the ammonium chloride crystals and gas such as argon is passed through the cell with defined relative humidity. (B) Schematic drawing of the redox process at the salt | electrode | gas triple phase boundary based on ion mobility across the salt crystal surface.

were performed with a μAutolab type III potentiostat (Ecochemie, NL). The scanning electron microscopy (SEM) images were obtained using a JEOL JSM6480LV system. Copper metal was identified with an energy-dispersive X-ray (EDX) analyzer. All experiments were conducted at a temperature of 22+/−2 °C in air unless stated otherwise.

2.3. Procedure for salt matrix voltammetry

The mechanical grinding of the salt mixture, ammonium chloride with the redox species of interest, was first carried out using a pestle and mortar until a fine uniform grain was obtained. The salt was then placed into the chamber of the electrochemical cell and the reference electrode and working electrode screwed into the base and top of the cell respectively until they were finger tight. Where argon gas flowed through the cell, humidity was kept constant by passing the gas through a gas wash bottle containing a mixture of solid NH_4Cl and a saturated aqueous solution of NH_4Cl.

3. Results and discussion

3.1. Salt matrix voltammetry I.: electrochemical characterization of water soluble redox systems on ammonium chloride

Initial experiments were conducted with the $Fe(CN)_6^{3-/4-}$ redox system. $K_4Fe(CN)_6$ when immobilised onto a NH_4Cl surface and placed into the electrochemical cell, shows well-defined redox responses (see Fig. 2A). Peak responses for oxidation and back-reduction are centred at a midpoint potential of 0.31 V vs. SCE and with a peak-to-peak separation of ca. 280 mV (at 10 mV s^{-1} scan rate). The midpoint potential and the peak-to-peak separation observed here are likely to be affected by the high ion activity at the surface of NH_4Cl crystals. The peak current increases with consecutive potential cycling (see Fig. 2A). The process is tentatively assigned to a one electron transfer (Eq. (1)).

$$Fe(CN)_6^{4-}(\mathrm{salt}) \rightleftarrows Fe(CN)_6^{3-}(\mathrm{salt}) + e^- \quad (1)$$

The data in Fig. 2B demonstrates the effect of the weight% content of the redox component $K_4Fe(CN)_6$ in the salt matrix. Although variations in peak currents from measurement to measurement

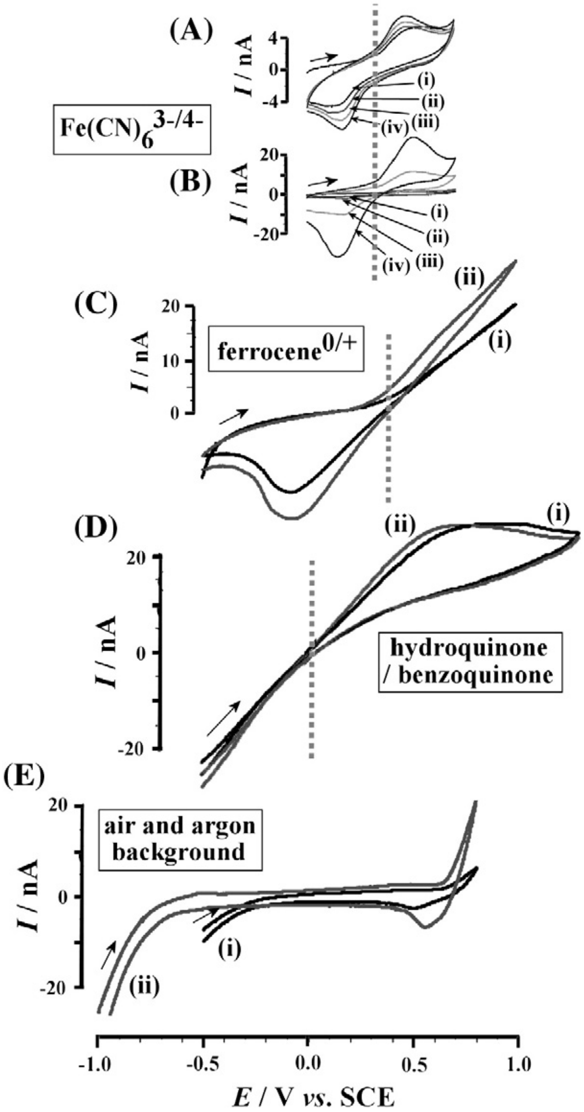

Fig. 2. (A) Cyclic voltammograms (scan rate 10 mV s^{-1}; scan 1 (i) to 4 (iv) shown) for the oxidation of 1 wt.% $K_4Fe(CN)_6$ immobilised into a NH_4Cl salt matrix and placed between a 2 mm diameter gold disc electrode and SCE counter/reference. (B) As before with (i) 0.1, (ii) 0.5, (iii) 1, and (iv) 2 wt.% $K_4Fe(CN)_6$ immobilised into a NH_4Cl salt matrix. (C) Cyclic voltammograms (scan rate 10 mV s^{-1}; scan 1 (i) and 2 (ii) shown) for the oxidation of 1 wt.% ferrocenedimethanol immobilised into a NH_4Cl salt matrix. (D) Cyclic voltammograms (scan rate 10 mV s^{-1}; scan 1 (i) and 2 (ii) shown) for the oxidation of 1 wt.% hydroquinone immobilised into a NH_4Cl salt matrix. (E) Cyclic voltammograms (scan rate 10 mV s^{-1}) for the NH_4Cl salt matrix (i) in air and (ii) in argon (relative humidity ca. 80%). Dashed lines indicate the approximate position of the reversible potentials.