



Electrochemical studies of processes occurring at the polycrystalline Cu electrode/methanol interface



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ABSTRACT

The electrochemical behavior of polycrystalline copper in 0.1 M LiClO₄ methanol solutions has been studied by means of cyclic voltammetry (CV), phase-selective AC voltammetry, electrochemical impedance spectroscopy (EIS) and scanning electrochemical microscopy (SECM). An investigation of the processes occurring during both positive and negative potential sweep directions is presented. The dependence of differential capacitance on potential, recorded by AC phase-selective tensammetric experiments, reveals surface reconstruction steps related to the formation/reduction of Cu(I)/Cu(II) methoxide surface films. Analysis of EIS data shows that methoxy anion adsorption/desorption takes place in an irreversible way, partially controlled by the diffusion of CH₃O⁻, while the transition from Cu(I) to Cu(II) surface film occurs in parallel to the dissolution of Cu(II) ions through the Cu(II) methoxide film also under mixed kinetic/diffusion control. The stability of surface films formed on the electrode surface has been studied via the SECM tip-substrate voltammetry technique. The obtained results suggest that the monovalent copper methoxide surface layer is stable, while the corresponding divalent copper film exhibits only partially inhibiting properties towards copper dissolution, since a considerable amount of dissolved copper ions was detected in the electrode vicinity.

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1. Introduction

The processes taking place at the interface between copper and methanol solutions are significant to the field of heterogeneous catalysis [1–4], since methanol can be employed as fuel in its pure form [5] or in a mixture with other liquid fuels (i.e. gasoline [6]). Moreover, methanol is the major alcohol used in transesterification and esterification processes of lipids and fatty acids respectively during biodiesel production [7]. Recent advances in the field of biodiesel production via heterogeneous catalysis routes, showed that copper in combination with other transition elements (Zn [8,9], V [10]) can serve as a promising catalyst material increasing the rate of esterification reactions. Copper-methanol interactions are also of interest in industrial applications since copper and copper-containing catalysts are potentially good catalysts for reactions such as the hydrogenolysis of glycerol to propylene glycol [11,12], the former being one of the main byproducts formed in biodiesel production plants. Furthermore, as long as hydrogen generation is a product of methanol steam reforming, copper-methanol interactions are important for fuel cell technology too [13,14].

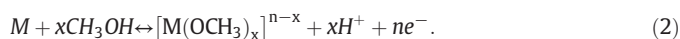
A literature survey of electrochemical studies on the interfacial behavior of copper and other metals, M, in methanol and ethanol has revealed several important contributions [15–19]. The general

conclusion is that, due to methanol self-dissociation, free methoxy anions react with the surface of metal M resulting to the formation of a [M(OCH₃)_x]^{n-x} layer, where n is the oxidation state of M in the film. Under the influence of electrode potential variation such surface layers undergo structural changes depending on the particular range of electrode potential and the direction of the potential scan.

The mechanism of anodic dissolution of metals in methanol can be summarized [15] as follows. Methanol as a protic solvent undergoes self-dissociation according to the reaction:



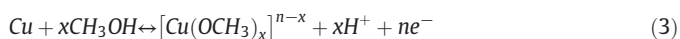
In methanol solutions, free CH₃O⁻ groups are involved in the reactions of anodic dissolution and cathodic deposition of various metals in a manner similar to the effect of OH⁻ ions in aqueous solutions. In particular, the presence of CH₃O⁻ ions in solution results to the methoxylation of the surface of a metal M [20–22], leading to the formation of surface films of the form [M(OCH₃)_x]^{n-x} according to the scheme:



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In the case of a Cu electrode in contact with methanolic solutions reaction (2) becomes:



where n is equal to either 1 or 2 depending on the oxidation state of Cu.

In the present work we investigate the interface of a polycrystalline Cu electrode in contact with neutral methanolic solutions, with an emphasis on the initial stages of oxidation (at intermediate potentials, prior to massive anodic dissolution) by means of cyclic voltammetry, phase sensitive AC voltammetry, electrochemical impedance spectroscopy (EIS) and scanning electrochemical microscopy (SECM).

2. Experimental/methodology

2.1. Electrode materials and chemicals

The Cu electrode serving as a working electrode was made of a copper rod (Good Fellow, 99.99+% trace metals basis) with a 3 mm diameter. The latter was sealed to the apex of a glass tube via a sleeve made of a shrinkable thermoplastic tube. Electrical contact was achieved by tin soldering of the electrode with a commercial copper wire. A Pt foil was utilized as auxiliary electrode. At its free end the Pt foil was bended so as to be parallel to the disk face of the working electrode at a distance of about 2 mm, in order to ensure uniform potential distribution. An aqueous Ag|AgCl electrode saturated with NaCl (Schott) was used, placed at a constant distance of 5 mm from the working electrode. The electrode arrangement was set in a single compartment double walled electrochemical cell kept at 298 K. Between each new set of experiments the Cu electrode was mechanically polished by abrasion with emery paper of decreasing grain size, followed by rinsing with distilled water and treatment for several minutes in an ultrasonic bath containing double distilled water. After the cleaning-polishing procedure and prior to each experiment the electrode was washed with the working solution and immediately transferred to the electrochemical cell, in order to avoid extended contact with air.

The Cu electrode used for the SECM experiments was assembled by embedding a copper rod (from the same material mentioned above) in a polyethylene disk base and sealing its end using epoxy resin. Again tin-based solder was utilized for electrical contacts. Prior to each experiment the same cleaning-polishing procedure described previously was followed. A Pt microelectrode (from Princeton Applied Research) with a 25 μm electrode diameter and a Pt tip-to-glass ratio (RG) of 10 was used as the amperometric sensor during SECM experiments. Before use, the Pt microelectrode was polished sequentially with 1, 0.3 and 0.05 alumina suspensions (Buehler) on a moistened polishing cloth, rinsed with copious amounts of distilled water, left to dry in air and finally washed with the working solution. The counter electrode was a Pt foil, while the previously mentioned Ag|AgCl electrode saturated with NaCl was used as a reference electrode.

Methanol (p.a. 99.8+%) from Chem-Lab Analytical and anhydrous LiClO_4 from Aldrich (99.99% trace metals basis) were used as solvent and supporting electrolyte respectively for all electrochemical measurements. $\text{CuNO}_3 \cdot 3\text{H}_2\text{O}$ (purum p.a. 98.0–103% RT) from Aldrich was employed for the preliminary study of Cu electrodeposition on Pt microelectrode, while ferrocene (98%) from Aldrich served as a mediator for SECM approach curve experiments.

2.2. Electrochemical procedures and setup

Electrochemical measurements were performed using an Autolab PGSTAT302N (EcoChemie) system equipped with the FRA32 module and controlled via Nova 1.11 software. Impedance spectra were recorded in deaerated solutions of 0.1 M $\text{LiClO}_4/\text{CH}_3\text{OH}$ in the frequency range of 5 kHz to 100 mHz. The amplitude of the AC perturbation signal was 10 mV. The reproducibility of all electrochemical impedance data was

confirmed by the comparison of several consecutive measurements at the same DC bias. The linearity-stability of EIS data was checked by the Kramers-Kronig test by which the complex, the real and the imaginary pseudo chi-square were found to be of the order of 10^{-5} to 10^{-6} in all systems studied and over all the frequency range. EIS data analysis was carried out by simulating the AC response of the theoretical equivalent circuits models and fitting the experimental data to the resulting equations by means of a complex nonlinear least squares (CNLS) technique, using Nova v.1.11 software (Metrohm Autolab) for minimizing the relative deviations of the simulated real and imaginary impedances from the experimental values. Moduli of calculated impedance values served as the statistical weighting and the resulting chi-square fitting parameter was found to be of the order of 10^{-3} in all systems over the experimental frequency range. Throughout the manuscript EIS parameters are presented normalized with respect to electrode substrate area.

Phase-selective AC voltammetric measurements were carried out by the experimental setup described previously [23], which comprises a lock-in amplifier (model SR830 from Stanford Research) and a potentiostat (model Potentiostat Wenking POS73 from Bank Elektronik), interfaced to a personal computer running LabVIEW 2013 SP1. The DC potential was applied in steps of 25 mV and each measurement was taken after a 5 s stopover period at each potential. The amplitude and the frequency of the AC signal were set to 4 mV and 80 Hz respectively.

SECM experiments were conducted at ambient temperature with a Princeton Applied Research Scanning Electrochemical Workstation (model M370) controlled via M370 software v.4.46. For the in situ electrochemical characterization of surface processes occurring at the Cu electrode (substrate), a custom made routine combining linear potential sweep and potential pulses was employed. Briefly, the basic steps followed are summarized below (for a detailed description see Section 3.4): By using the bi-potentiostat mode, the substrate was subjected to a typical linear sweep voltammetry experiment at a relatively low scan rate (in order to attain quasi-steady state conditions) promoting the various reactions on its surface. Simultaneously a Pt microelectrode (tip), placed at a specified distance above substrate (via approach curve experiments, see Section 3.4), was biased at a fixed potential suitable for monitoring changes on substrate surface (see below for a detailed description). Working solutions were deaerated, while during each SECM experiment N_2 was continuously purged in the cell (leading to a constant N_2 blanketing of the solution) to ensure the complete absence of oxygen in the working solutions.

3. Results and discussion

3.1. Surface electrochemistry of Cu electrodes

Fig. 1 shows the cyclic voltammetry of Cu electrodes in deaerated methanolic solutions of 0.1 M LiClO_4 at a scan rate of 100 mV s^{-1} . After immersion of the electrode into solution, the initial potential (set at -1.30 V vs Ag/AgCl to attain a clean, free of oxides electrode surface) was immediately applied and the electrode was scanned towards the positive potential limit. The stabilized voltammogram of Fig. 1 was established after repetitive cycling between -1.3 V vs Ag/AgCl and $+0.3$ V vs Ag/AgCl for ca 20–30 potential cycles. In the positive scan direction, anodic waves can be clearly seen, most likely corresponding to the Cu(0)/Cu(I) at ca -0.5 V vs Ag/AgCl and Cu(I)/Cu(II) at ca -0.2 V vs Ag/AgCl transformations [15,16], while the reverse sweep gives rise to their cathodic counterparts related to the reduction of the oxidized species.

In more detail, a surface film of $\text{Cu}(\text{OCH}_3)_{\text{ads}}$ is readily formed after the introduction of the Cu electrode in the methanolic solution (reaction (4) - chemisorption), followed by the formation of a $[\text{Cu}(\text{OCH}_3)_2]^-$ film of Cu(I), stable in the anhydrous methanol

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