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First principles of hot-tip scanning electrochemical microscopy: Differentiating substrates according to their thermal conductivities

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ABSTRACT

The use of ac polarized microelectrodes in the arrangement for scanning electrochemical microscopy is described. Application of a high frequency ac waveform to a microelectrode tip results in a resistive heating of the surrounding electrolyte solution and the onset of the electrothermal flow. We report that the presence of a substrate in close proximity to the hot tip leads to a substantial change of the temperature in the hot zone, which in turn results in a measurable effect on the shape of the recorded approach curves. Thus, the observed changes in the faradaic current, measured with the tip, can be used to distinguish substrates according to their thermophysical properties, namely, thermal conductivity. Experimental data are shown to be in good agreement with the results of the theoretical simulations. This work exemplifies initial findings obtained with a novel technique that is termed Hot-Tip Scanning Electrochemical Microscopy (HT-SECM).

1. Introduction

Heated (or hot) microelectrodes have proved to be very useful in many areas of electroanalysis [1–3]. This fact can be explained by a number of positive effects of localized heating on electrode processes, such as the enhancement of mass transport, acceleration of reaction kinetics, improvement in selectivity of detection due to the thermal discrimination of analytes, and an electrode 'cleaning' effect [4–8]. Besides being used as electrochemical microsensors, hot microelectrodes have also been applied to the detection in capillary electrophoresis [9–11]. However, until now no examples have been given in the literature on the use of hot microelectrodes in the arrangement for the Scanning Electrochemical Microscopy (SECM). An explanation could be that there is no other sufficiently easy and convenient way of heating microelectrodes for this purpose, but by applying a high frequency ac waveform to a disk microelectrode using an ac signal generator. This method has been initially developed by Baranski [12] and later expanded by Boika and Baranski [4,13].

SECM is a powerful and versatile analytical technique, with which it is possible to probe the topography of samples, measure heterogeneous reaction rates of the processes taking place at solid–liquid and liquid–liquid interfaces, study kinetics of coupled chemical reactions and modify a substrate locally by electrochemically generated reagents [14].

SECM measurements at variable temperatures have attracted some attention previously from a number of groups [15,16]. Schäfer et al. described a setup capable of performing temperature controlled SECM studies [17]. Their approach was based on the use of the Peltier element as the heating device, and thus required the heating of the whole solution in a custom made SECM cell. This is different from what we are proposing in the presented paper. By using ac heating of a tip in HT-SECM one only heats a small volume of solution in close proximity to the electrode, thus not affecting the temperature in the bulk of the cell. As a result, the heating rate is much higher, and the heating practically does not affect the signal-to-noise ratio [12], as opposed to the method of Schäfer et al. (in their case, the heating pulses applied to the Peltier element had to be synchronized with current acquisition in order to improve the signal-to-noise ratio). In addition, application of a high frequency ac waveform to a microelectrode tip also leads to the electrothermal flow of solution, which causes higher rates of mass transfer compared to heating alone [4,13]. This is beneficial for kinetic studies, in which one is required to have a high rate of mass transfer in order to be able to extract kinetic information.

In this work we show the possibility of HT-SECM measurements and demonstrate that by using this technique one is capable of differentiating materials according to their thermal conductivities. We support our experimental findings by the results of theoretical simulations, thus providing further details on the complexity of phenomena observed in the SECM gap due to high frequency ac heating.

2. Material and methods

2.1. Electrochemical cell, samples and chemicals

The electrochemical cell consisted of a 10 μm diam. Pt disk working electrode (RG = 5; RG = r_g/a, where r_g is the radius of the insulating sheath and a is the electrode radius), a Ag|AgCl|KCl (2 M) reference electrode, and a counter electrode made of 0.3 mm platinum wire.

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Fabrication of microelectrodes was done according to a well-established procedure [4]. Alumina sample was purchased from MTI Corporation, Richmond, CA (item number ALCeramic101005S2, purity 96%). Polystyrene sample was prepared by compression molding using a compression molding press (CARVER 4122, Wabash, IN) at 493 K. All solutions were prepared using Millipore water and ACS grade chemicals. Electrochemical measurements were done without the removal of dissolved oxygen.

2.2. Instrumentation

Instrumental setup used in the experiments consisted of a commercially available Scanning Electrochemical Microscope (model CHI 920d, CH Instruments, Austin, TX) interfaced with a custom-built ac signal generator (courtesy of Prof. A. S. Baranski), a low-pass filter and the described above electrochemical cell. The schematic of the filter is shown in Fig. 1.

The design of the filter is similar to the one already published [4], with the main difference being that an ac waveform (from the signal generator) is supplied through a transformer U1 (part number PE-65968NL, Pulse Electronics Corporation), the use of which reduces noise. Printed circuit board for the filter was designed using Fritzing open-source software (www.fritzing.org) and produced manually using “PCB Fab-in-a-Box” kit from Pulsar Professional (Digi-Key part number 182-1027-ND). The ac signal generator used in the experiments had the nominal power output levels of 14, 17, 20 and 23 dBm, and the frequency range 35 to 4400 MHz. The microtranslation stages of the SECM, the signal generator, the filter and the electrochemical cell were all positioned inside a custom-built grounded Faraday cage in order to minimize the effect of an external electromagnetic interference on experimental results. In addition, all cables leaving the Faraday cage had ferrite filters on them in order to minimize potential electromagnetic leakage.

3. Theory/calculation

Numerical simulations of the presented HT-SECM experiments were done using a model developed with COMSOL Multiphysics software (v5.2). The following phenomena were considered and simulated: (1) the heating of an electrolyte solution by a high frequency ac waveform applied to an SECM tip, and the resultant temperature distribution, (2) the electrothermal force and the flow of solution, and (3) the mass transfer of the redox species with an accompanying reversible faradaic reaction at the tip. This model is similar to the one published previously by Boika and Baranski [18]. However, the main differences are that in the present work we accounted for the effect of solution convection on temperature distribution, as well as the temperature dependence of the properties of the heated electrolyte solution (density, heat capacity and thermal conductivity). The simulations also accounted for the effect of temperature on the magnitude of the diffusion coefficients of the redox species (due to the change in the solution viscosity), and the presence of the substrate in close proximity to a hot tip. It should also be noted that in simulations of mass transfer we take into consideration the presence of the Soret diffusion (also known as nonisothermal, or thermodiffusion) [19]. The value of the Soret coefficient for ferrocyanide ions was taken equal to $5.15 \times 10^{-3}\ \mathrm{K}^{-1}$, and $1.41 \times 10^{-3}\ \mathrm{K}^{-1}$ for KCl, as reported by Snowdon and Turner [20].

4. Results and discussion

4.1. Experimental findings

The experimental results presented here were obtained in the following two typical SECM experiments: an approach curve experiment, in which a microelectrode (tip) is brought by SECM microtranslation stages towards a studied surface (substrate) while recording the faradaic current corresponding to the oxidation of the redox species (ferrocyanide ions), and a mapping experiment, in which the tip is scanned over the surface of a sample at a constant height thus giving the faradaic current map of the substrate. At room temperature the magnitude of the measured faradaic current is indicative of the electrical properties of the surface, i.e., if it is electrically insulating (negative feedback is observed) or conductive (positive feedback is observed). With HT-SECM we set out to investigate if we could distinguish materials based on their thermophysical properties, namely the thermal conductivity. The underlying idea is that if two substrate materials have different thermal conductivities and, in addition, are both electrically nonconductive, then by using a hot tip one would expect to observe a difference in the shapes of the approach curves due to an additional heat transfer from the hot zone around the tip into the more thermally conductive substrate (note that at room temperature the experiment produces identical approach curves).

Before any HT-SECM measurements could be performed, we had to determine an optimum ac heating frequency. This was done by recording the faradaic current corresponding to the oxidation of ferrocyanide ions as a function of the frequency of the applied ac waveform, with the tip electrode positioned in the bulk solution far away from the surface of a substrate. Obtained current–frequency curves showed the presence of a maximum, which is indicative of the previously described *LC*-resonance (*L* — inductance, *C* — capacitance) [4]. Thus, for the heating experiments with HT-SECM one could essentially choose any frequency in the studied range 100–200 MHz. However, we chose

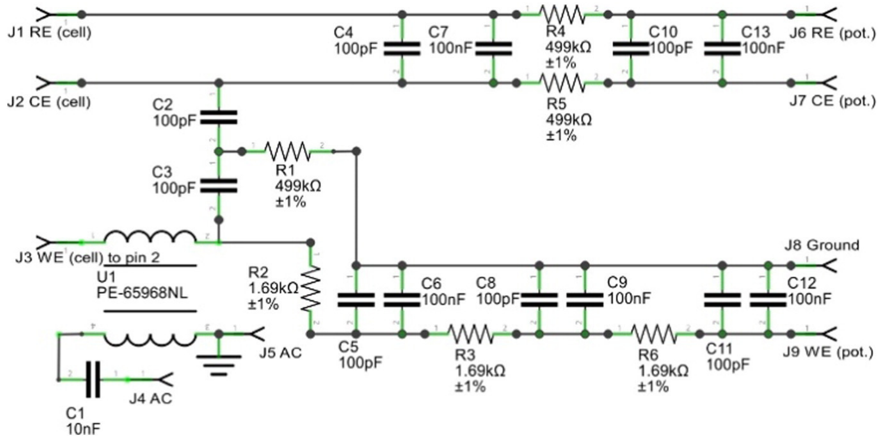

Fig. 1. Schematic diagram of a filter used in the experiments. Pins J1, J2, and J3 were used to connect the filter to the reference, counter and working electrodes, respectfully, in the cell; J4 and J5 were used for connection of the signal generator, while J6, J7 and J9 connected the filter to the reference, counter and working electrode inputs of the SECM potentiostat; pin J8 was used to connect the filter to the instrument ground.