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Disposable thermostated electrode system for temperature dependent electrochemical measurements

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ABSTRACT

We describe the fabrication of a screen printed disposable electrode system with integrated elements to allow for control of the working electrode temperature. The device has fully functional working, counter, and reference electrodes with underlying thermocouple and heating elements to allow feedback control of temperature. In our experiments, we determined that the accuracy of the temperature measurements on the electrode was within 0.5 °C over the temperature range of liquid water using a single universal calibration, and we demonstrated that the control system could maintain a setpoint temperature with a root mean squared error of 0.35 °C based on the indicated temperature. We used these electrodes to determine the temperature dependence of the diffusivity of ferricyanide ($[Fe(CN)_6]^{3-}$) ion using linear sweep voltammetry. The diffusion coefficient determined at 25 °C (0.85×10^{-5} cm^2 s^{-1}) was similar to other reported values in the literature, although our observed activation energy for diffusion (32.1 kJ mol^{-1}) was significantly higher. Our observed temperature coefficient of −1.63 mV K^{-1} for the redox potential of the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ couple is reasonably close to other reported values. The system shows promise for use in other disposable electrochemical diagnostic systems in which temperature control plays a key role, especially where perturbations or variations in ambient temperature or electrolyte rheological properties make feedback control necessary.

1. Introduction

Incorporation of temperature control on instruments and sensors is commonly practiced to enable data collection on a variety of different temperature dependent physico-chemical processes [1], or to optimize the performance of chemical sensors with respect to sensitivity, power dissipation, and other characteristics [2]. Our ultimate objective is to develop a disposable thermostated electrode platform for use in a DNA based bacterial diagnostic system, which would allow for simple isothermal replication of target DNA [3] to lower the detection limit and allow for control of the hybridization conditions to improve the stringency of an electrochemically mediating hybridization reaction [4,5]. A variety of system designs for conducting electrochemical experiments at elevated temperatures have already been described in the literature [6–13], and have been proposed for studying a wide range of systems including corrosion at high temperatures, the design of more efficient/powerful batteries and fuel cells, and improvement in the sensitivity of electrochemical detection systems. Increasingly, heated electrodes are becoming more miniaturized to make them more practical for bioanalytical applications [14–28]. Heating in these systems has been done by direct resistive heating of the electrode [14,17–19,21,22,24,26,28], resistive heating of an element directly underlying the electrode [23,25], and irradiation with microwave [15,20], radiofrequency [16], or laser energy [10,11,27]. These systems typically operate in a non-isothermal condition where the microelectrode is heated directly without perturbing the bulk solution, for example to prevent denaturation of heat labile molecules [27] yet still enhance the sensitivity particularly through thermal convection. One drawback of these systems is that typically the temperature control signal is initially calibrated against well characterized thermo-electrochemical behavior on the electrode, but the actual temperature control is open-loop and so susceptible to error with changes in the ambient conditions or the thermal/rheological properties of the electrolyte. To achieve our objective on a low cost platform with feedback control, we have attempted to reproduce simple screen printing protocols for tem-

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perature sensitive elements directly on the electrode. Conceptually, similar control systems have been incorporated onto pulse oximeter electrode systems for the amperometric detection of blood oxygen levels [29,30]. In these systems, screen printed metal films performed a dual function, both as a resistive heater and as a feedback element to determine the electrode temperature. Given the difficulty in printing resistive elements with a tight degree of tolerance and the corresponding constraints for having to develop separate calibrations for each "disposable" electrode, our approach was to print thermocouple elements onto the electrode system for temperature sensing as these rely on material properties and result in more easily reproducible characteristics between electrodes. Various strategies for depositing simple thermocouple based temperature sensors onto a substrate have been developed [31,32], and reproducible performance is easily achieved. In this work we used silver and nickel as the thermocouple pair as materials which were readily obtainable in ink form, exhibited a reasonably sensitive and highly reproducible thermoelectric response, and were compatible with simple screen printing materials for making gold electrode surfaces.

2. Numerical modeling

2.1. Electrode power dissipation

In the interest of designing an electrode system with as low required heating power as possible, numerical modeling of the electrode system was undertaken for a variety of geometries and alumina compositions prior to designing the electrodes. On the basis of these simulations, we selected a 91% alumina substrate (ADOS-90, Coorstek, Grand Junction, CO, USA) which has about half the thermal conductivity of higher alumina content substrates ($13\,W\,m^{-1}\,K^{-1}$ at 20 °C compared to $26\,W\,m^{-1}\,K^{-1}$ for 96% alumina) [33], rolled as thin as practically possible (0.01 in. or 0.254 mm thickness). Simulations were carried out using structured scripts written in a math solving software (MATLAB 7.4, The MathWorks, Natick, MA, USA) to implement an implicit finite difference method [34] to determine transient and steady state temperature distributions. These simulations were validated by solving the same physical system with a commercial finite element software (COMSOL Multiphysics, COMSOL Incorporated, Burlington, MA, USA). In both simulation methods the electrode itself was considered to be composed solely of the substrate (i.e., the effects of the printed layers were neglected), it was assumed that the working electrode surface was kept uniformly at the setpoint temperature, and that a perfectly efficient heat sink was applied to the electrode contacts (i.e., the edge touching the heat sink was regarded as a constant temperature surface at ambient temperature). All other surfaces were regarded as experiencing natural convective heat loss to the ambient air, assuming the electrode was oriented in a horizontal plane with the working electrode face up and using convective heat transfer coefficients calculated for horizontal surfaces [35]. Steady state heating power requirements were determined by numerically integrating the convective heat losses along the surface of the electrode and conductive losses into the electrode base/heat sink. These simulations were compared to the dissipated power measured on a real electrode oriented horizontally in an undisturbed enclosure.

Due to complexities in modeling the electrode in contact with a test solution, uncertainty in optimal configuration of the solution with respect to the electrode, and how to handle transients in heating up a finite volume of solution, no attempt was made to model the power under these conditions. However it was noted that steady state heating requirements for electrodes in solution were similar to those recorded for electrodes in air once the test solution was uniformly brought to temperature.

3. Materials and methods

3.1. Electrode fabrication

Thermostated electrodes were made on the selected alumina substrate using a manual screen printer (model HC-53, Affiliated Manufacturers Inc., North Branch, NJ, USA) to print commercially prepared silver, gold, nickel, resistive, dielectric, and overglaze coating inks (products 9912-K, 8831-UF, 2554-N1, 29106, 4920, and G-481, respectively, ESL ElectroScience, King of Prussia, PA, USA). The sequence of patterned layers applied to the alumina sheet to form a single device is shown in Fig. 1. Patterned screens for the screen printing process were custom fabricated (Sefar, Northridge, CA, USA). Electrodes were designed to incorporate a small annular resistive heater (~1 mm diameter, 0.1 mm wide trace) directly underlying but electrically isolated from the working electrode, and a thermocouple was made to directly measure the working electrode temperature using a silver/nickel pair. The silver trace and contact of the thermocouple was also used as a contact for the working electrode for performing electrochemical analysis. Gold was used for the working and counter electrodes, and silver was used for the reference electrode. The final overglaze layer was used

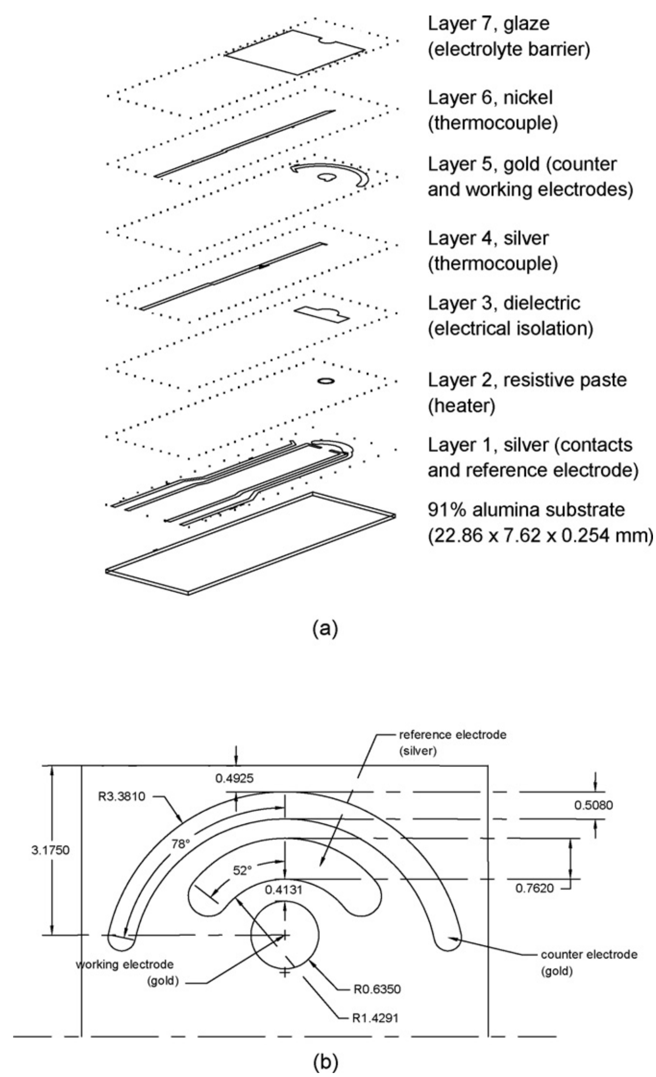

Fig. 1. (a) Screen printed patterns applied for the preparation of disposable thermostated electrodes, and; (b) dimensional drawing of the electroactive surfaces of the disposable electrode (all dimensions in mm).