ASSESSMENT OF ELECTROCHEMICAL PROPERTIES OF A BIOGALVANIC SYSTEM FOR TISSUE CHARACTERISATION

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Abstract

Bio galvanic characterization is a promising method for obtaining health-specific tissue information. However, there is a dearth of understanding in the literature regarding the underlying galvanic cell, electrode reactions and their controlling factors which limits the application of the technique. Our findings suggest that the prominent reaction at the cathode is that of oxygen-reduction, not hydrogen-evolution. Results indicate that cell potentials are influenced by the concentration of dissolved oxygen at low currents and maximum closed cell currents are limited by the rate of oxygen diffusion to the cathode. Characterized internal resistance values for the salt solutions did not correspond to theoretical values at the extremes of concentration (1.71 and 154 mM) due to electrode resistance and current limitation. Existing bio galvanic models do not consider these phenomena and should be improved to advance the technique and its practical application.

Keywords: Biogalvanic, Tissue resistivity, Zinc–copper galvanic cell, Oxygen-reduction reaction, Tissue sensing

1. Introduction

There is a clinical need in many medical interventions to obtain specific information regarding the health of biological tissues. This is particularly pertinent to minimally invasive surgery, where the loss of haptic feedback has limited the information available to the surgeon during a procedure. Research spanning a number of sensing modalities has looked to address this problem. Such proposed techniques include: determination of tissue mechanical properties through force sensing surgical probes [1] or ultrasound based elastic imaging [2]; time-dependent electrical properties in the field of Bioimpedance Spectroscopy (BIS) [3]; and most recently chemical composition analysis through near-real-time spectroscopic analysis of cauterised tissue vapour [4], [5]. Although research within these modalities has shown potential, some application-specific issues remain making alternative sensing strategies desirable. In addition, aggregation of multiple sensing modalities can often lead to an improved depiction of the region of interest through exploitation of the individual technique strengths. biogalvanic characterisation technique proposed by Golberg et al. [6] combines electrochemical and electrical principles to allow passive determination of a tissue's resistive properties. Dissimilar metal electrodes (copper and zinc) are coupled to the tissue of interest creating a galvanic cell. Subsequent connection of the system through external resistors allows regulation of cell current (I). The voltage measured across the external resistor (R_{EXT}) can be applied to a mathematical model of the system (Eq. (1)) allowing an internal resistance (R_{INT}) to be determined. Extension of this technique proposed by Chandler et al. [7] uses a full set of measured voltages across the range of external resistors to allow more accurate determination of the internal resistance. In addition, this technique allows the Open Circuit Voltage (OCV), which is the potential difference between the galvanic cell electrodes when no current flows, to be determined without direct measurement.

For characterisation, a zinc and copper galvanic cell is established and used as the current generating power source with the cell current being passively regulated using external resistors. This reduces measurement system complexity as external power supply and current control electronics are not required, in contrast to BIS measurement. The simplicity of the biogalvanic method makes it an attractive sensing modality. However, with the infancy of this technique comes a dearth of scientific understanding. Previous application to porcine tissues *ex vivo* and *in vivo* showed sensitivities to mechanical contact condition (strain levels) and resistor switching direction as well as presenting unexpected transient currents between resistor switching [7]. In addition, and crucially, little is known of the electrochemistry that governs the characterisation process.The actual half-cell reaction potentials are influenced by the cell conditions in accordance with the Nernst equation, where the actual reduction potential, E_{red} is a function of the standard half-cell reduction potential E^0 and the chemical activity of the reducing agent, a_{red} and the oxidising agent, a_{ox}. For dilute solutions the activity coefficient tends to unity leaving the chemical activity interchangeable with ionic concentration. For the hydrogen evolution reaction (Eq. (3)) to be thermodynamically favourable at pH 7, a potential more negative than − 0.41 V (SHE) is required at the cathode. The measured Open Circuit Potential (OCP) of copper under comparable conditions, and measured in this study is + 0.1 V (SHE), making hydrogen evolution unfavourable [9]. The oxygen reduction reaction (Eq. (5)) at pH 7 is however thermodynamically feasible at potentials lower than + 0.81 V (SHE), suggesting that this is the primary reaction at the copper cathode under open cell conditions. Therefore the full cell reaction within the galvanic cell would be that of Eq. (6) Biogalvanic characterisation within the range of expected tissue resistivity (0.2–50 Ωm [10]) using the proposed external resistance range will necessitate moving the cell from near open cell conditions towards short circuit. For high current levels the electrode potential must shift away from the equilibrium potential by an amount ΔV, in accordance with the Tafel Eq. (7). The term α represents the charge transfer coefficient and the terms F, R and T represent the Faraday constant, the universal gas constant and absolute temperature, respectively [11]. The sign within Eq. (7) indicates the reaction type with positive representing an anodic process and a negative representing a cathodic process. It is possible that the required potential shift for the cathodic reaction supporting the anodic dissolution of the zinc metal will become sufficient to cause change from solely oxygen-reduction to a mixed system also including hydrogen-evolution.

1.2. Corrosion considerations

The measurement system is fundamentally based on the corrosion of zinc metal. As such, the corrosion mechanisms for zinc dissolution as well as the supporting cathodic reactions should be considered. Electrochemical studies have been conducted looking at zinc and copper in isolation, and as part of a galvanic cell. In neutral and basic solutions the anodic polarisation of zinc produces oxides and hydroxides, although passivation of the electrode is not achieved [12]. García-Antón et al. [13] suggest that these oxide regions may cause reduced reaction kinetics for the zinc oxidation reaction. This could lead to increasing resistance of the zinc electrode with time. However, shorter time scales and surface treatment between tests should mitigate or at least reduce the effect of this potential issue. Cathodic polarisation of copper in neutral aqueous solution will be dominated by the reduction reactions of water and of dissolved oxygen; Eqs. (3), (5), respectively. In particular, the rate of the oxygen-reduction reaction, Eq. (5), has been shown to be limited at a high overpotential by the mass transport of dissolved oxygen to the electrode surface [14]. As part of a Zn–Cu galvanic couple, the copper electrode has been shown to be highly polarisable with respect to the zinc electrode [15]. Therefore the behaviour of the copper electrode under cathodic polarisation will be likely to dominate the behaviour of the galvanic cell.

1.3. NaCl solution model

In order to characterise the electrochemical properties of the system, tests have been conducted within salt solutions (NaCl (aq)) of varied concentration. This offers improved control over the system parameters in comparison to testing with biological tissue. In particular, a salt solution model allows control over the salt bridge conductivity giving meaningful validation to the biogalvanic characterisation system. The applicability of using an aqueous sodium chloride system is based on a number of assumptions: (1) the primary tissue current pathway is through extracellular fluid, (2) the dominant ionic components of extracellular fluid are Na^+ and Cl^-, and (3) the electrochemistry is dominated by the NaCl medium and the electrode properties. It is common within BIS characterisation to consider biological cells in a capacitive nature, due to their non-conductive lipid bilayer cell membrane [16], [17]. At low frequency the current pathway will therefore be predominantly through the extracellular fluid surrounding the cells. The major ionic species within extracellular fluid are Na^+ and Cl^- making the use of NaCl solution an appropriate model [16], [18]. Initial comparisons between the NaCl solution and tissue results have been made within this study to understand further the efficacy of this model. The analysis of a salt solution system can thus help to validate the biogalvanic system and demonstrate the influence of electrochemical factors that may need to be addressed for reliable use in tissue characterisation. Specific testing of OCV, closed cell currents and transition currents was undertaken. This paper reports the influence of salt solution conductivity within a physiological range on these independent aspects of the galvanic cell. Additionally, comparisons have been made between the independent electrochemical findings and the applied characterisation process, with reference made to published tissue data.

4.3. Galvanic characterisation

The internal resistance values predicted using the biogalvanic characterisation method show discrepancies with theoretical values determined using conductivity data for the corresponding solution concentrations. For the 1.71 mM solution, the measured internal resistance is much lower than theory (25%). This is due to the method of characterisation not being specific to the internal resistance, and thereby measuring the influence of electrode activation. For the 154 mM solution, internal resistance values were measured as being larger than those predicted theoretically. This can be accounted for through the mass transport limited current under closed cell conditions being a dominant factor over the solution resistance. In addition the characterised resistance is highly variable within the same conductivity of solution which corresponds with the fluctuation seen at closed cell current levels. The resistance of the electrodes are also not accounted for within the characterisation model which will inevitably lead to a larger prediction of internal resistance if the system is assessed over the full current range. The internal resistance determined of the 17.1 mM solution shows agreement with theory, and also indicates little variation with repeat testing.

5. Conclusions

There are potential benefits to biogalvanic characterisation although application of this modality requires repeatable and accurate results across a range of operating conditions. To fully assess the efficacy of this method, tissue assessment incorporating the findings presented in this paper is of primary importance. Mitigation of the issues demonstrated may be achieved through optimisation of the characterisation system, specifically selection of electrode material and geometry, and through appropriate selection of external resistive loads to limit the cathodic overpotential to the activation and internal resistance control regimes, thereby avoiding current limiting oxygen diffusion effects. Additionally, inclusion of the OCV parameter during assessment may yield more reliable metrics pertaining to tissue health, as this parameter is linked to the known variations in tissue oxygen concentrations..

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