Electrochemistry Communications 75 (2017) 82–85

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Alternating current-bipolar electrochemistry

Vera Eßmann [a], Jan Clausmeyer [a,1], Wolfgang Schuhmann [a,*]

[a] Analytical Chemistry - Center for Electrochemical Sciences (CES), Ruhr-Universität Bochum, Universitätsstr. 150, 44780 Bochum, Germany

ARTICLE INFO

Article history:
Received 1 December 2016
Received in revised form 23 December 2016
Accepted 6 January 2017
Available online 8 January 2017

Keywords:
Bipolar electrochemistry
Alternating current
AC frequency
Rotating bipolar electrode
Electrochemiluminescence

ABSTRACT

Rotation of a bipolar electrode in a constant electric field between feeder electrodes causes an alternating bipolar current at an AC frequency that depends on the rotation rate. The corresponding oscillation of the feeder current is evaluated by means of a lock-in amplifier. This innovative approach allows the current flowing through the non-wired bipolar electrode in an open bipolar system to be extracted without relying on electrochemical reporter reactions.

1. Introduction

Instead of electrically connecting an electrode to a potentiostat, it is possible to apply electrode potential differences in a non-wired manner using bipolar electrochemistry (BPE) [1,2]. A bipolar electrode (BE) is a conductive object of any shape or size placed between two feeder electrodes that are utilised to apply a constant electric field to the solution (Scheme **1**a) [3]. By adjusting to one potential within the gradient of solution potentials around it, the BE is divided into two poles with prevailing anodic and cathodic overpotentials, respectively. If the feeder voltage V_{app} is sufficiently high, charge transfer may occur at both poles. Importantly, the BE potential E_{BE} is adjusted to balance oxidation and reduction currents. The interfacial potential differences change gradually along the BE, thus allowing gradual electrodeposition or electrodissolution. BPE has previously been utilised for the analysis of thickness [4,5], composition [6,7], and corrosion [8] gradients. In other studies, the two BE extremities were heterogeneously modified resulting in even microscopic Janus particles [9]. Since anodic and cathodic BE currents have to be equal to maintain electroneutrality, the current through the non-wired electrode can be read out if one reaction provides an optical signal. In this regard, *e.g.* quantification of the anodic dissolution of Ag has been reported [10]. However, measurement of electrochemiluminescence (ECL) is the most widely used method of quantifying the bipolar reactions. ECL of oxidative luminophores such as $[Ru(bpy)_3]^{2+}$ or luminol has been detected with a photomultiplier (PMT) or a CCD camera and the resulting data used to draw conclusions about the corresponding reduction reaction at the other pole of the BE [1,11,12] To quantify anodic redox reactions, reductive fluorophores such as resazurin have been applied [13].

Alternating current (AC) methods in electrochemistry can be used to quantify the influence of various independent processes on the overall response of complex electrochemical systems. In-phase amplification of current signals upon applying AC stimuli is widely used in square-wave and pulse voltammetry to boost the sensitivity of electroanalytical detection. However, AC methods have been little used in BPE, presumably due to the large time constant of the feeder electrodes, which prohibits fast reversal of the electrode potential. An approach using alternating current in a non-wired, coiled electrode, which employed ECL for quantification and the number of coils to control the potentials, has been developed using wireless energy transmission instead of feeder electrodes to apply alternating potentials [14].

We extend the scope of BPE by applying effective AC potentials to the BE to derive the bipolar current i_{BE} from the feeder current i_{feeder} in an open bipolar system without any optical read-out reactions. For analytical applications using an open and static bipolar configuration, where the BE and the feeder electrodes are located in the same compartment, i_{BE} cannot be extracted from i_{feeder}, because i_{feeder} would also increase upon analyte addition. This intrinsic limitation can be overcome by bringing i_{BE} to oscillation with a certain frequency (alternating bipolar current) through rotation of the BE in the DC electric field between the feeder electrodes. The same oscillation is then observed in i_{feeder}, thus making it a carrier of the analytical signal.

2. Material and methods

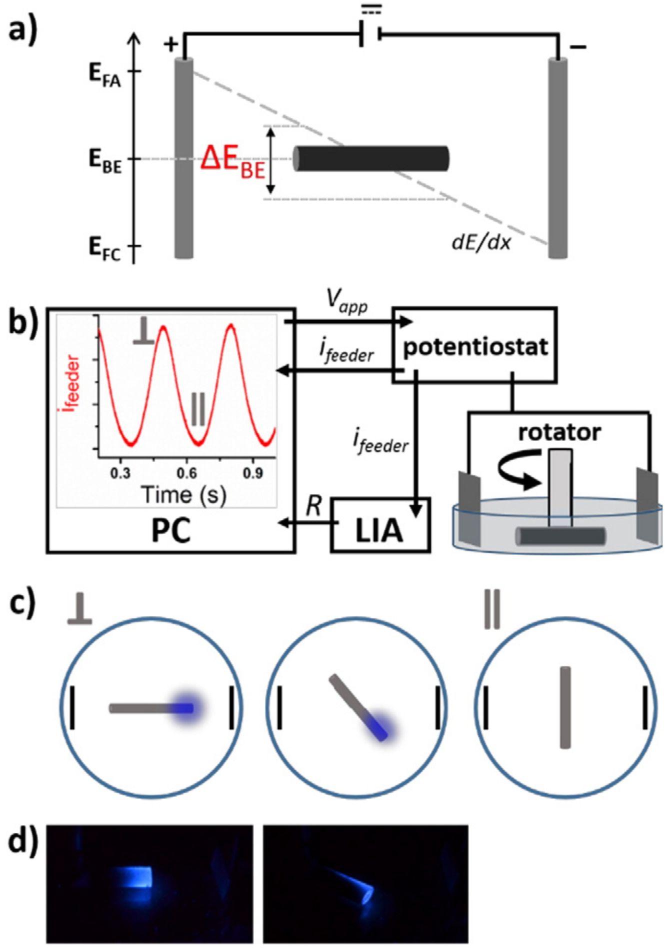
A graphite rod 40 mm long and 6 mm in diameter was used as the BE. It was positioned between two stainless steel feeder electrodes

---

* Corresponding author.
E-mail address: wolfgang.schuhmann@rub.de (W. Schuhmann).

[1] Current address: University of Texas at Austin, Department of Chemistry and Biochemistry, 105 E 24th St. Stop A5300, WEL Hall 2.204, Austin, TX 78712-1224.

http://dx.doi.org/10.1016/j.elecom.2017.01.006
1388-2481/



Scheme 1. a) Schematic depiction of the fundamental principle of BPE. b) Schematic experimental setup with dependency of i_{feeder} and c) ECL on the orientation of the BE. The BE is located between the two feeder electrodes and attached to a RDE rotator. When oriented orthogonally to the feeder electrodes (⊥), i_{feeder} is highest. It is lowest when the BE is oriented in parallel (∥). d) Photos (Nikon D7000) of luminol ECL at the anodic pole of a stationary BE in different orientations at $V_{app} = 4$ V.

that were located in a petri dish at a distance of 83 mm. For rotation, the BE was attached to a RDE rotator (Metrohm) and rotated at 100 rpm. All measurements were performed in 50 mL 0.1 M borate buffer (BB, pH 8.5, H_3BO_3, AppliChem and NaOH, VWR) prepared with ultrapure water (SG water) and containing 5 mM luminol (ABCR) and varying amounts of H_2O_2 (VWR). Voltages between the feeder electrodes were applied using a potentiostat (IPS, controlled by a Visual Basic-based software program called "Union" which was developed in-house). Being connected to the signal input of a lock-in amplifier (DSP, model 7280, Signal Recovery, AC gain 6 dB), the current signal i_{feeder} was synchronised with the reference channel to obtain the magnitude R. The reference frequency corresponding to the rotation rate was generated by the internal oscillator of the lock-in amplifier (oscillation frequency 3.2 Hz).

To insulate the BE for the control measurement, commercial nail varnish was used. V_{app} was swept from 0 to 6 V and back at 50 mV s^{-1} using a H_2O_2 concentration of 0.12 M while monitoring i_{feeder} and its magnitude.

A video of the RBE rotating at 100 rpm in 0.1 M BB (pH 8.5) with 5 mM luminol and 0.1 M H_2O_2 was recorded with an EMCCD camera (Evolve Delta 512, Photometrics, gain = 400) while 3.5 V were applied to the feeder electrodes. In the frames, the feeder cathode is seen at the top. The video is played back at 10 frames per second.

3. Results

To demonstrate the concept of alternating current-bipolar electrochemistry (AC-BPE), a simple and flexible setup based on model reactions was designed (Scheme 1). An anisotropic BE, meaning a conductive object with different x- and y-dimensions, such as a graphite rod, is rotated using a RDE rotator at constant speed between two feeder electrodes applying an electric field. In contrast to previous studies involving rotating BEs (RBEs) [15–20], the potential drop across the length of the BE, ΔE_{BE}, is periodically changed to induce an oscillation of i_{BE}. In this study, redox reactions only serve to show the modulation of the bipolar current and thus the feeder current with rotation. Luminol was therefore used only to additionally visualise the interfacial potential drop across the BE and to follow the rotation. Note that ECL is not required in this case to quantify the BE processes. The total current between the feeder electrodes can be carried through the solution by ion transfer (i_{ion}) and through the BE by electron flow (i_{BE}). The ratio between i_{ion} and i_{BE} depends on the solution resistance, R_S, the BE resistance, R_{BE}, the charge transfer resistance R_{CT} of the BE, as well as on the potential drop across the BE, ΔE_{BE}, to overcome R_{CT} and induce faradaic processes. This potential drop correlates with the BE orientation. When the BE is oriented orthogonally to the feeder electrodes (Scheme 1, ⊥), the value of ΔE_{BE} is at its maximum, which implies the maximum contribution of i_{BE} to the total i_{feeder}. This can also be seen from the high ECL intensity recorded for an orthogonal BE orientation (Fig. 1d). According to the gradual interfacial potential difference, the ECL intensity is highest at the extremity of the anodic pole and decreases toward the middle. In the case of a parallel orientation, a negligible current flows through the BE, leading to a minimum in i_{feeder}. No ECL is observed as ΔE_{BE} is insufficient to drive faradaic reactions. Consequently, i_{feeder} comprises i_{BE}. To enable low-noise current amplitude monitoring, the rotation frequency was used as the reference signal of a lock-in amplifier, which extracts the in-phase modulation of the oscillating i_{feeder} signal. The magnitude of the output R is used as a measure of the signal oscillation (given in volts). The AC signal is free of the large DC background current passed between the feeder electrodes in an open BPE setup. Moreover, the use of a lock-in amplifier allows the elimination of noise from i_{feeder}.

To confirm that i_{BE} can be deduced from the lock-in amplifier magnitude R, faradaic currents were increased stepwise by addition of H_2O_2 aliquots. The applied feeder voltage for optimal discrimination of the magnitude R at different H_2O_2 concentrations was assessed by sweeping V_{app} between 0 and 6 V and back at 10 mV s^{-1} in the presence and absence of 0.1 M H_2O_2. The most significant differences were obtained for voltages larger than 2.5 V. For the following potentiostatic experiment, a value of 3.5 V is considered to be the optimal balance between sufficiently high reaction rates and the prevention of side reactions starting at higher potentials. At the beginning of the measurement in the absence of H_2O_2, i_{feeder} oscillates around ~1.45 mA with a magnitude of 0.083 V (Fig. 1a). From the current signal as recorded with an oscilloscope (Scheme 1b, model WaveSurfer 44MBs-B, Teledyne LeCroy) and as recorded with the potentiostat (Fig. 1a, inset, 20 ms acquisition rate) it can be seen that one period, corresponding to 0.5 revolutions as the BE has two poles, takes 0.3 s in accordance with the rotation rate of 100 rpm. The addition of H_2O_2 aliquots leads to a stepwise increase in faradaic current at the feeder electrodes as well as an increase in i_{BE} as seen from the increase in average i_{feeder} and in the magnitude R, respectively. A calibration curve was obtained by plotting the magnitude value *vs* the H_2O_2 concentration (Fig. 1b).

It should be borne in mind that i_{feeder} also oscillates when no faradaic reactions occur at the BE. This background oscillation can be ascribed to the ionic current that is partially hindered by the RBE to a periodically varying extent. Also, the capacitive current at the BE changes with the orientation to the feeder electrodes *i.e.* with ΔE_{BE}. To assess the background oscillation amplitude of the ionic current, an insulated BE was rotated while a voltage ramp was applied to the feeder electrodes