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Journal of Power Sources

journal homepage: [www.elsevier.com/locate/jpowsour](http://www.elsevier.com/locate/jpowsour)

# Revisiting methods to characterize bioelectrochemical systems: The influence of uncompensated resistance ( $iR_u$ -drop), double layer capacitance, and junction potential

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## H I G H L I G H T S

- Junction potential,  $iR$ -drop and capacitive current bias electrochemical measurement.
- These are rarely considered in bioelectrochemical systems (BES).
- In typical BES setups  $iR_u$ -drop can shift measured potentials by more than 200 mV.
- More than 40% of the current can originate from the double layer capacitance.
- Methods to quantify the  $R_u$  and double layer capacitance are discussed.

## A R T I C L E I N F O

### Article history:

Received 31 December 2016

Received in revised form

6 March 2017

Accepted 7 March 2017

Available online xxx

### Keywords:

Bioelectrochemical systems

Electrochemical methods

$iR$ -drop

Uncompensated resistance

Double layer capacitance

*Geobacter sulfurreducens*

## A B S T R A C T

Bioelectrochemical systems (BES) are characterized with methods derived from the electrochemistry field, for e.g. linear sweep voltammetry (LSV), cyclic voltammetry (CV), and chronoamperometry. The limitations of electrochemical measurements are well known and described, but there are new challenges when these are applied to biological systems. For instance, the electrolyte conditions are pre-defined by the application involving the use of low conductivities, leading to an increase of two error sources: the  $iR_u$ -drop and junction potential. Furthermore, the use of electrodes with high surface areas and thus high double layer capacitance lead to capacitive currents that superimpose the biocatalytic current of interest. Even though these problems have often been mentioned in the bioelectrochemistry field, they are seldom considered and reported in publications. The scope of this work is to present and discuss methods to quantify the  $R_u$  and double layer capacitance, and to demonstrate their significant influence on the recording of polarization curves. In a typical BES setup, it is exemplarily shown that due to  $iR_u$ -drop measured potentials can deviate by more than 200 mV from the actual potential. Similarly, more than 40% of a recorded electrode current can originate from the electrode material's double layer capacitance.

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## 1. Introduction

The term microbial bioelectrochemical system (BES) includes several emerging technologies in which electrochemical redox reactions are catalyzed by living microorganisms such as electroactive bacteria. Research in this field has grown steadily over the

last decade, since it offers sustainable technologies for the generation of electricity or valuable chemicals from waste products such as sewage, biomass, or CO<sub>2</sub>. Furthermore BES can also be used for bioremediation and biosensing [1].

As any electrochemical cell, BES comprise two electrodes, anode and cathode. At the anode, electroactive microorganisms usually transfer electrons released upon the oxidation of a substrate to the electrode. From here, the electrons flow through an external electrical circuit to the cathode, where an electron acceptor is reduced. In a microbial fuel cell this is usually oxygen, which is reduced to

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water. Due to the negative Gibbs free energy of the overall reaction, the electrons flow spontaneously from the anode to the cathode, and electrical energy is generated in the process. In a microbial electrolysis cell, protons or water are used as an electron acceptor at the cathode, to produce molecular hydrogen. The Gibbs free energy of this reaction is positive, so an additional voltage must be applied between the anode and the cathode to drive the process. Depending on the used electron acceptor, the imposed additional voltage, and the catalyst, different products like acetate, ethanol, methane, 1,3-propanediol, or even complex biochemicals such as pharmaceuticals [2,3] can be obtained at the cathode.

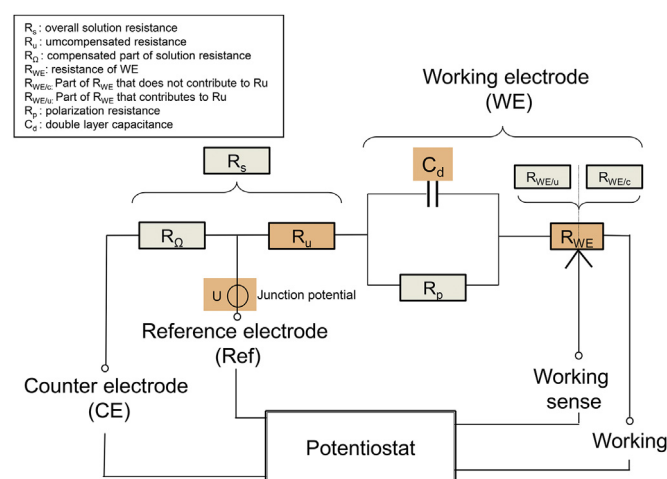
To characterize BES, standard electrochemical methods such as polarization curves, linear sweep voltammetry (LSV), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) are used [4]. However, in BES their application is not straightforward, since in this case the catalyst is a biological and dynamic system that is not yet fully understood, and can very much be influenced by the chosen characterization method. Furthermore, the characteristics of the electrolyte are predefined by the application (for instance wastewater with low conductivity) and cannot be changed towards values that would be optimal for the intended characterization method. Accordingly the need for standardization, especially on careful selection and application of characterization methods, has often been emphasized [4–7]. Of particular importance is the uncompensated resistance ( $R_u$ ) which can result in a large potential deviation between measured and actual electrode potential ( $iR_u$ -drop) in experiments with low conductivity electrolytes such as wastewater. Furthermore, capacitive currents resulting from high surface area electrode materials superimpose the faradaic current related to microbial activity [7]. Both effects can extremely falsify results. Nevertheless, in current literature they are rarely considered in a quantitative way. A third potential issue is the occurrence of junction potentials between working and reference electrodes that can falsify the measured electrode potential.

The aim of this work is to quantitatively investigate the influence of uncompensated resistance and electrode double layer capacitance on the polarization data recorded under typical operation conditions of BES. Thereto, the different methods to determine uncompensated resistance are compared in two different standard setups with different electrodes and electrolyte conductivities. It is shown, that both, the choice of method and the electrode arrangement have a significant influence on the measured uncompensated resistance. Furthermore, the double layer capacitance of typical electrode materials relevant in the field of BES was determined. In addition, the strong impact of electrode capacitance and uncompensated resistance on polarization data is analyzed in a quantitative way, highlighting the necessity to consider both effects in the study of BES. Finally, methods to determine or avoid the junction potential are discussed so that electrode potentials can be translated to vs. the SHE reference electrode, and be compared amongst different studies.

This work focuses on three electrode arrangements, as they are a powerful setup to study electrode performance without limitations concerning the counter electrode. Nevertheless, the results and methods are equally relevant to two-electrode setups and whole electrochemical cells.

## 2. Origin and determination of capacitive currents, uncompensated resistance, and junction potential

In the following section, the theoretical background of capacitive currents, uncompensated resistance, and junction potential as part of the electric equivalent circuit of a three-electrode setup (Fig. 1) is introduced, and suitable methods for their determination



**Fig. 1.** Electric equivalent circuit for a three-electrode setup. The uncompensated resistance  $R_u$  leads to a deviation of the WE potential from the set potential. The double layer capacitance  $C_d$  can contribute to a significant share to the measured current when using dynamic characterization methods and the electrical resistance of the electrode causes a non-uniform potential distribution across the electrode. The highlighted components and their influence on polarization curves will be discussed in the following sections of this paper.

are discussed. The electric equivalent circuit has been developed according to [8]. Compared to the simplest equivalent circuits, it has been extended by the working electrode's resistance and its splitting into a compensated and an uncompensated part (see section 2.2: Influence of the working electrode resistance and contacting), and the junction potential (see section 2.3).

### 2.1. Double layer capacitance

The double layer capacitance ( $C_d$ ) arises from the charge accumulation at the electrolyte/electrode interface [9] and will contribute to the recorded current whenever dynamic electrochemical methods such as LSV, CV or linear current sweeps are used. The contribution of the capacitive current,  $i_c$ , which is not related to a bio-electrochemical reaction, can lead to a significant overestimation of the performance of a BES electrode. In particular when using highly porous materials with a large double layer capacitance, the capacitive current can be considerably higher than faradaic currents that originate from the bioelectrochemical electrode reaction [8].  $C_d$  generally depends on the type of electrode material, the composition of the electrolyte and its ionic strength, the temperature, and the electrode potential [10]. When using LSV to characterize an electrode, a potential ramp is applied at a specific sweep rate  $\nu$  (in  $\text{V s}^{-1}$ ). This will result in the following current [8] consisting of a capacitive part and an ohmic dampening part:

$$i = \nu C_d \left( 1 - e^{-t/R_u C_d} \right) \quad (1)$$

The contributing resistance in Eq. (1) depends on the setup, and can be assumed as the uncompensated resistance  $R_u$  in a three-electrode setup. For simplicity reasons, only  $R_u$  of the solution is considered. Also, the electrical resistance of the working electrode can contribute to  $R_u$ . At a typical sweep rate of  $1 \text{ mV s}^{-1}$  [4] an estimated capacitance of  $C_d = 1.5 \text{ F}$  for a  $1 \text{ cm}^2$  activated carbon electrode, and  $R_u$  as  $50 \text{ } \Omega$  for the electrolyte resistance, the behavior of the capacitive current will be as shown in Fig. S1A (supplementary). In this example,  $1.5 \text{ A m}^{-2}$  will originate from abiotic capacitance. For comparison, LSV with an electrode with a much smaller capacitance of  $0.8 \text{ mF cm}^{-2}$ , such as graphite felt, will result

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