

Subtractive Kinetic Investigations of Electrode Reactions in a Mixed PEM Electrolysis Cell

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Electrical performance of an electrochemical cell operating either as water electrolyser or as mixed cell for oxygen consumption from the fed air stream is presented. Utilization of PEM-electrolyser technology can explain that the performance is better in electrolyser configuration. Operating temperature slightly improves the yields. For photobiological applications, the cell would be used as oxygen regulator of the CO₂ enriched vapor phase. The present investigation validates that the presence of CO₂ in air stream does not affect the cell performance. Steady voltammetry and impedance spectroscopy performed for the two configurations allow to deduce, in a first part, kinetics of oxygen evolution in electrolyser mode, considering hydrogen evolution from the literature. The case of mixed cell operation was thereafter considered, using the deduced law for the anode. Subtracting the anode part from the overall response of the cell led to estimate for the kinetic law of oxygen reduction. The cathode resistance calculated from the law is in good agreement with the cathode resistance determined from EIS.

1. Introduction

Photobioreactors are used in a large field of applications. In the aerospace area, Ai et al. (2008) developed a photo-bioreactor which can produce algae protein as food and provide oxygen. For pharmaceutical applications, León-Bañares et al. (2004) improved nuclear transformation of microalgae in order to improve the production of value-added metabolites and proteins. Microalgae are also useful for the production of renewable energy since they can be converted to biodiesel. Chisti (2007) explained that from 1 to 3% of the total US cropland would be devoted to produce algal biomass that satisfies 50% of the transport fuel needs, in comparison to oil palm cultivation which requires 24% of the total cropping area. But perhaps the most important application of photobioreactors is carbon dioxide removal from gaseous effluents (Ai et al., 2008, Chisti, 2007, and Demirbas, 2011). Biocapture of CO₂ by microalgae is a permanent and reliable solution for CO₂ removal compared to temporary and unsafe solutions e.g. capture or storage technologies. Growth and efficiency of microalgae is influenced by the dissolved CO₂ concentration in the aqueous phase, and by nutrients and light intensity. Nevertheless, photosynthesis generates oxygen which inhibits photosynthesis at high concentration (Molina et al., 2001). Bubbling CO₂ is a common method to remove accumulated oxygen and to increase dissolved CO₂ concentration (Chai and Zhao, 2012). The drawbacks of bubbling CO₂ are large CO₂ lost into the atmosphere (Putt et al., 2011), more power consumption for operation, and algal cell damage. This consumption results in increased CO₂ concentration in the air and consequently in water according to Henry's law. Besides the principle of an electrochemical process to decrease oxygen concentration in air had been suggested and validated experimentally (Eladeb et al., 2012). This versatile cell of PEM technology involves oxygen evolution by water anode oxidation and oxygen consumption at the cathode. After a brief presentation of the cell, its electrical performance with and without carbon dioxide in the fed air stream is given. Kinetics of oxygen consumption was deduced by electrochemical impedance spectroscopy measurements: the cell was first operated as water electrolyser to deduce kinetics of oxygen evolution considering the kinetic law for hydrogen evolution from the literature. The case of mixed cell operation was thereafter considered, using the obtained law for the anode reaction to estimate the kinetic law for oxygen reduction.

2. Working conditions influence

2.1 Versatile cell presentation

A 25 cm² PEM cell originally designed for water electrolysis has been tested as water electrolyser and also as mixed cell working with water and air feed in the anode and cathode compartments respectively (Eladeb et al., 2012). Nafion® 117 membrane acts as both electrolyte and separator of the two chambers. Figure 1 presents the material involved in the cell.

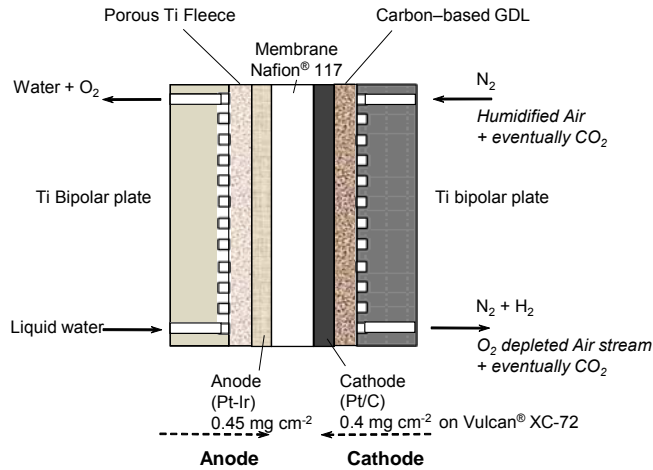


Figure 1: Schematic view of the cell. At the cathode, circulating gas are written in upright characters in electrolyser mode and in italics in mixed cell mode.

Whatever the configuration, water oxidation occurs at the anode side (Eq(1)):



At the cathode, hydrogen is created in electrolyser mode (Eq(2)) and oxygen is reduced in mixed cell mode (Eq(3)):



The open circuit voltage should be equal to 1.20 V at 60 °C in electrolyser and to zero in mixed cell mode.

2.2 Polarization curves and temperature influence

Polarization curves were carried out in H₂O/N₂ and H₂O/air configuration at constant stoichiometry for gas stream at the cathode ($\lambda_{\text{gas}} = 3$). Whatever the experimental conditions, the anode compartment was always fed with 5 cm³ min⁻¹ liquid water. Experiments were conducted at 60 °C and 80 °C to study the temperature effect on the electrical performance. Reactants were preheated before entering the cell. For polarization curves, the current density was maintained constant until cell voltage stabilization.

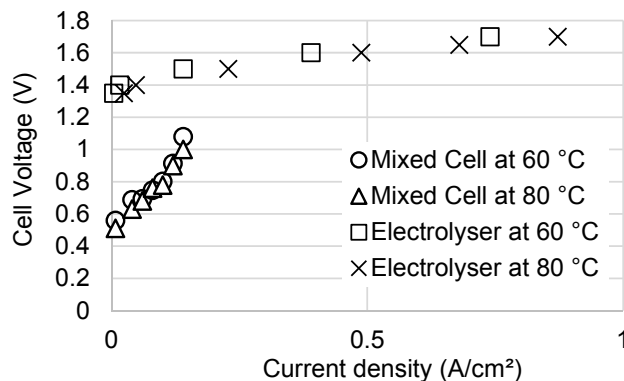


Figure 2: Polarization curves for the two configurations at 60 and 80 °C.

Figure 2 shows polarization curves for the two modes (electrolyser and mixed cell) and for the two temperatures studied. Electrolyser mode exhibits better performance than the mixed cell. Overpotentials at non-zero currents are larger in this latter configuration. Use of PEM-electrolyser technology can explain that materials are more suitable in electrolyser mode. Water electrolysis and oxygen reduction are slightly accelerated at higher temperature. As a matter of fact ion transport and electron transfer processes as thermal activated processes allow reduced overpotentials.

2.3 CO₂ at the cathode in mixed cell mode

Utilization of the electrochemical cell for oxygen regulation in a photobioreactor requires that the cell components would not prematurely age with carbon dioxide present in the vapor phase. The mixed cell was thus submitted to CO₂-enriched air (2 % in volume, Andersen (2005)) for 55 h as presented Figure 3. The current density was fixed at 0.14 A cm⁻² and the temperature at 60 °C. Dioxide Carbon injection in air stream did not affect the cell performance and consequently its components by corrosion or other parasite reactions. Current efficiency of oxygen reduction was close to unity in all tests made (Eladeb et al. 2012.)

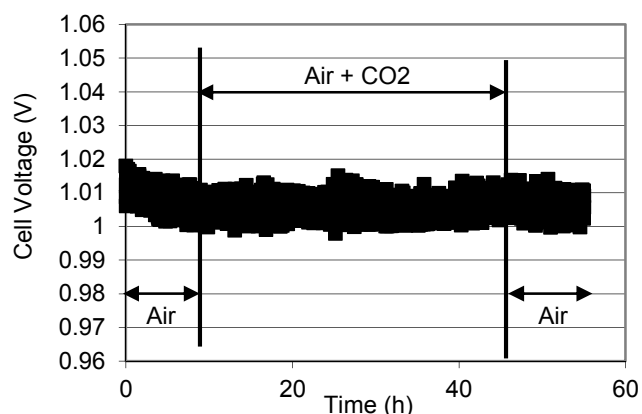


Figure 3: Voltage of the mixed cell submitted to CO₂ in air stream

3. Electrochemical section

3.1 Impedance spectroscopy measurements

Measurements were carried out using a potentiostat (Autolab[®]) connected to an 20 A booster (Autolab[®]). Amplitude of the sine perturbation was fixed at 10 % of the steady current for sufficient accuracy of the low frequency part of the spectra. Frequencies were scanned from 10 kHz to 100 mHz, with 10 points per decade. Fitting the spectra to the theoretical impedance of the cell, established from the electrical equivalent circuit presented in a previous paper (Bonnet et al., 2008), should yield estimation of the ohmic resistance at high frequency and for zero imaginary part of the impedance, the charge transfer resistance at the anode and cathode sides in the high-middle frequency range and the diffusion resistance at the cathode in the low frequency domain.

The main objective of this part is to determine the kinetic law of oxygen reduction in the mixed cell configuration. However, as reactions are a mirror image of each other in this cell, their overpotentials should be of the same order of magnitude. In the impedance spectra, the two loops related to anode and cathode kinetics are probably of the comparable significance, so are their characteristic frequencies. As a matter fact, the two contributions in the EIS spectra cannot be distinguished from the overall charge transfer loop (data not shown). Therefore, it was preferred to determine kinetics of oxygen evolution at the anode in electrolyser configuration considering kinetics of hydrogen evolution at the cathode side from the literature. The very different overpotentials for H₂ and O₂ evolution limits the uncertainty of the method.

3.2 Kinetics of hydrogen evolution in electrolyser mode

Determination of kinetic parameters of hydrogen evolution reaction (HER) on platinum surface has been the topic of numerous investigations. However, for electrolyzers of PEM technology, very few reliable data are available. A literature survey on overpotentials of HER on platinum surfaces in acidic media shows that the average Tafel slope in the current density range 0.01-0.5 A cm⁻² is of the order of 60 mV/decade, according to the expressions established by Tavares (2001), whereas, according to Quaino et al. (2007) and Conway and Bai (1986), the average Tafel slope would be closer to 40 mV/decade, as shown by

Figure 4. For the present work, it has been preferred to consider the average numerical law (Eq(4)) being a compromise between the laws proposed in the above cited investigations:

$$\eta_{H_2\ Evol} = -0.027 + 0.13 * i^{0.26} \tag{4}$$

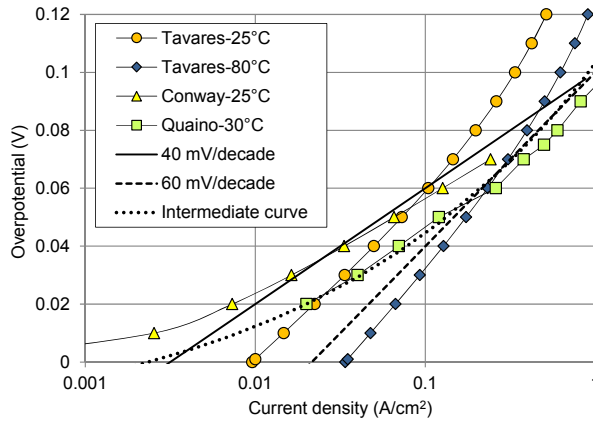


Figure 4: Overpotentials of HER vs. cd. on Pt surface: comparison of various literature data and Eq(4).

3.3 Kinetics of oxygen evolution in electrolyser mode

For estimation of the anode overpotential, the polarization curve of the cell recorded at 60°C has been treated by subtraction of:

- The reversible voltage, equal to 1.20 V at 60°C;
- The ohmic drop, directly related to the cell resistance, which was determined from the impedance spectra at high frequency at 0.007 Ω, i.e. 0.175 Ω cm⁻² (Figure 5). Because liquid water in a large excess is fed to the anode, it can be assumed that the membrane hydration is the same whatever the current density applied. Millet et al. (2011) measured the ohmic resistance of a Nafion 117 membrane at 0.15 Ω cm⁻²;
- The overpotential of hydrogen evolution, using Eq(4).

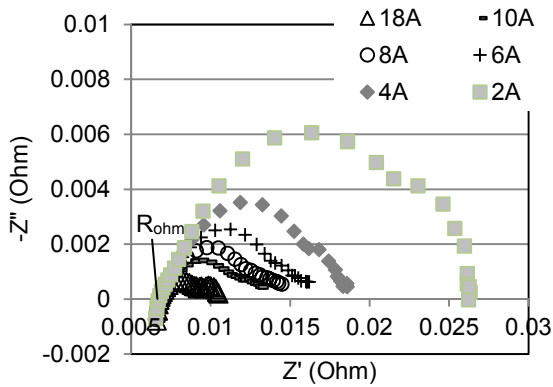


Figure 5: Impedance spectra for water electrolysis in the 25 cm² cell.

As shown by Figure 6, the obtained values for anode overpotential are consistent with data reported by Millet et al. (2011) and Biaku (2008), obtained from treatment of i-V variation of a 6 kW electrolysis stack. Fitting of our data, for current density below 1 A cm⁻² led to the following relationship:

$$\eta_{O_2\ Evol} = 0.017 * \ln\left(\frac{i}{1.2 * 10^{-5}}\right) \tag{5}$$

where $\eta_{O_2\text{Evol}}$ is in V and i in $A\text{ cm}^{-2}$ which corresponds to a Tafel slope near 40 mV/decade. The exchange current density, estimated to $1.2 \cdot 10^{-5} A\text{ cm}^{-2}$ is far lower than that for hydrogen evolution, which is in good agreement with most conclusions reported in published works on water electrolysis.

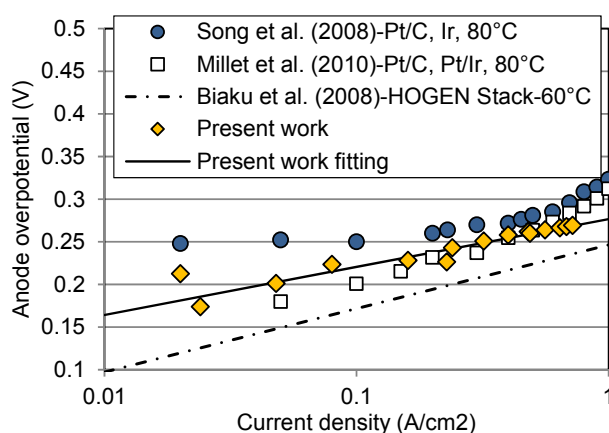


Figure 6: Estimated overpotential for oxygen evolution on Ir-based materials versus cd .

3.4 Kinetics of Oxygen reduction in mixed cell mode

As explained above, the cell voltage is the sum of the equilibrium voltage, the ohmic drop and the absolute electrode overpotentials. In the present case the reversible voltage might be expected to be zero, since anode and cathode are used for reactions reverse from each other. In fact the cell voltage at zero current has been often measured at approx. 350 mV, likely caused by the existence of a redox couple caused by one poorly isolated cell component. In any case, regular examination of the cell structure for membrane replacement did not reveal traces of corrosion; neither did chemical analysis of the water fractions collected at the cell outlet. The additional source of irreversibility in the system is a penalty for the energy performance, however without affecting its environment. Beside this additional voltage, the ohmic drop calculated on the basis of the above $0.17 \Omega\text{ cm}^{-2}$ and the anode overpotential have been subtracted from the overall cell voltage, leading to the cathode overpotential. The empirical law for the oxygen reduction could be established from the experimental data as:

$$\eta_{O_2\text{Red}} = 0.1 * \exp(10.99 * i) \quad (6)$$

The resistance for this reaction can be calculated by derivation of the overpotential after Eq(7):

$$R_c = \left(\frac{di}{d\eta_{O_2\text{Red}}} \right)^{-1} \quad (7)$$

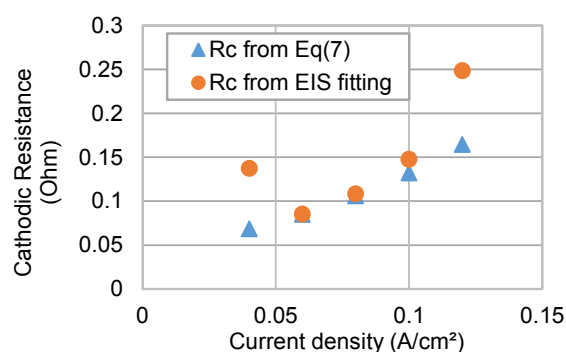


Figure 7: Cathodic resistances obtained by calculations or by fitting of EIS spectra.

Figure 7 shows the values for the cathode resistance obtained by applying Eq(7) and those determined by fitting of the experimental EIS. For fitting of the spectra, the two loops for charge transfer and diffusion phenomena were often lumped, with the presence of a slight shoulder only, so the two resistances could

not be distinguished from each other. Therefore in some cases, possible contribution of the diffusion part might be contained in the estimated for the charge transfer resistance. Nevertheless, good agreement between the values for charge transfer resistance of the air cathode is shown in Figure 7, except for two data, for the above reasons. The empirical laws for anode and cathode overpotentials could then be validated, so could be the equivalent electrical circuit used for fitting of EI spectra.

4. Conclusions

An electrochemical versatile cell fed with water at the anode compartment and with nitrogen (electrolyser mode) or with air (mixed cell mode) at the cathode was presented. As this cell can be employed for oxygen consumption from to the gaseous phase to be fed to a photobioreactor, the cell was submitted to carbon dioxide presence in air stream. The voltage measurement at fixed current for 40 h evidenced the CO₂ has no effect on the cell components. From the polarization curves obtained in water electrolysis, the kinetic law of the oxygen evolution was deduced. Anode overpotentials calculated from our measurements and those obtained in the literature were in the same order. The oxygen evolution kinetic law was then used in the mixed cell mode to deduce the kinetic law of oxygen reduction. The cathode resistance calculated from the law was compared to the resistance determined from the impedance spectra and found in good agreement.

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