Review Article

Electrochemical impedance spectroscopy as a tool to investigate the electroreduction of carbon dioxide: A short review

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ABSTRACT

Carbon dioxide electroreduction (CO$_2$ER) exploited in conjugation with renewable energy sources can open the path to a carbon-neutral energy cycle, concurrently offering the possibility to synthesize low-carbon fuels. In the last decades, a huge amount of work has been carried out by the scientific community in order to obtain high-performing and low-cost catalysts, and to design reactors able to maximize the efficiency of CO$_2$ER. Electrochemical impedance spectroscopy (EIS) proved to be a useful tool in studying this electrochemical reaction, and has been widely employed to characterize novel materials and reactor architectures. The aim of this Review is to provide an insight on the application of EIS for the study of CO$_2$ER. A brief introduction on the technique and on the reaction will be given, followed by a review of the most important applications in this field. Finally, a brief discussion of future research directions will be presented.

1. Introduction

Despite some eccentric denier theory, climate changes and global warming represent two of the most important problems humanity has to face in the next future [1]. It is widely accepted in the scientific community that anthropogenic activities are the main responsible for these issues [2]. The effect of human actions is particularly manifest from the increase of the concentration of greenhouse gases (GHGs) in the atmosphere: in fact, starting from the industrial revolution, the concentration of carbon dioxide has increased of about 40% [3], leading to the current value of 400 ppm [4]. In order to limit this effect, in 1998 United Nations developed the Kyoto Protocol [5], which established to reduce the human emission of GHGs by at least 5% with respect to level reached in 1990; in 2011 the European Union fixed as objectives for 2020 to reduce its GHG emissions by 20%, to increase energy production from renewable sources to 20% and to reduce overall energy consumption by 20% [6]. However, according to the Paris Agreement signed in December 2015, that imposes to limit the global warming below 2 °C by the end of this century [7], the reduction of carbon dioxide emission alone is not sufficient: it is necessary therefore to think to solutions able to remove CO$_2$ from the atmosphere and to store it, eventually using it as reagent to obtain added-value products (hydrocarbons, alcohols, etc…) [8].

In this context, CO$_2$ reduction reaction (CO$_2$RR) demonstrated to be promising toward a carbon-neutral energy cycle. This reaction can be mainly carried out through chemical methods, or through photo- and electro-catalytic routes. Concerning the latter, a lot of interest has been demonstrated by the scientific community, thanks to numerous benefits, including repeatability and controllability of the process, compactness and up-scalability of the reactors, and possibility to use green chemicals such as water or wastewater as supporting electrolytes [9]. Indeed, in last years, a huge and increasing number of papers has been published on this topic [10]. All the components related to CO$_2$ electroreduction (CO$_2$ER) are currently investigated, including catalysts [11–15] and electrolytes [16–20], but also new set-up and architectures [8,21,22] for characterization and exploitation of novel materials.

In this framework, Electrochemical Impedance Spectroscopy (EIS) has been demonstrated to be a useful tool for the study of the charge transfer and transport processes involved in this reaction [23,24], as well as for the characterization of materials [12,25–27] and reactors [28–30]. Generally speaking, EIS measurements can be carried out in all of those systems in which the ionic conduction is prevalent on the electronic one [31], including electrolytes [32–34], glasses [35–37], polymers [38–40], or devices, such as fuel cells [41–43], batteries [44–46], or solar cells [47,48], and for a large variety of applications, including corrosion [49,50]. For a comprehensive dissertation about impedance spectroscopy, the reader is invited to consult References [31,51–53]. Briefly, EIS technique is based on the application of a sinusoidal voltage $V(\omega,t)$ (to which a constant voltage could be also superimposed) with variable frequency f ($f = \omega/2\pi$, where ω is the angular frequency) to the system under study and on the measure of the current response $I(\omega,t)$ to this perturbation. The resulting impedance $Z(\omega,t)$ can

be calculated through the Ohm's law as:

$$Z(\omega, t) = \frac{V(\omega, t)}{I(\omega, t)} = |Z(\omega)|\, e^{j\theta} = |Z(\omega)|(\cos\theta + j\sin\theta)$$

$$= Z'(\omega) + jZ''(\omega) \tag{1}$$

where $|Z|$ is the impedance modulus, θ is the impedance phase, j is the imaginary unit, and $Z'=|Z|\cos\theta$ and $Z''=|Z|\sin\theta$ are the real and the imaginary part of the impedance, respectively. Since usually in electrochemical systems charge transfer and transport processes exhibit well-defined characteristic time constants, by exploiting this frequency-based technique it is possible to analyze them in details. Two different representations are usually exploited for presenting EIS data. The first one reports Z'' as a function of Z' in the complex plane, and it is referred to as Nyquist plot, while the second one, called Bode plots, consists of a pair of graphs reporting $\log|Z|$ and θ as a function of $\log f$. It has to be highlighted that in the Nyquist representation it is best practice to depict both axes with the same scale, in order not to induce artificial deformations which could mask the actual electrochemical behavior, and reporting some frequency points, in order to provide information about the time constants involved in the processes. Quite often, experimental data coming from impedance measurements is fitted through an equivalent electrical circuit (EEC), which is composed by elements (resistances, capacitances, etc…) that mimic the electrical behavior of the system under study, or of one of its parts. The results of the fitting procedure can give quantitative information about the processes involved in the reaction.
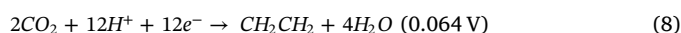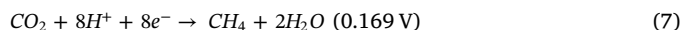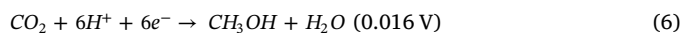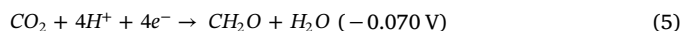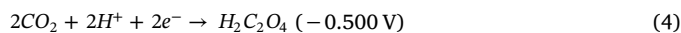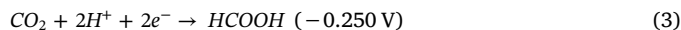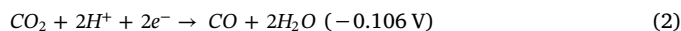
All the above reported considerations justify the need for a collection of the most important results obtained in this field. Thus, in this article, the application of EIS in CO₂ electroreduction studies is reviewed. It is worth noticing here that in a large part of the published literature on this topic, impedance involvement is limited to a qualitative analysis (*i.e.* no EECs are exploited for the quantification of the electrical parameters), or it is incomplete, often regarding only resistance contributions. In such cases, EIS studies could originate partial or mistaken interpretations of the observed phenomena, thus failing in their goal to help in casting light on CO₂ electroreduction process. Throughout the manuscript, some examples of these incomplete/incorrect investigations will be provided, highlighting their weak points. Summing up the above reported concepts, the aim of this review is to give scientists working on this field an overlook on the possibilities of application of this technique for the study of these electrochemical systems. Accordingly, the paper is subdivided as follows: Section 2 briefly presents the fundamentals of CO₂ electroreduction; Section 3 is devoted to the application of EIS in the study of materials, while particular applications are reviewed in Section 4; Section 5 provides a general conclusion based on the previous sections, together with a brief discussion of future research directions.

2. CO₂ electroreduction

Electrochemical reduction of CO₂ is an unfavorable process, mainly because this molecule is extremely stable and inert from a thermodynamic point of view [8]. For this reason, high-performing and long-lasting catalysts are required, in view of a technological commercialization. Currently, in fact, the slow kinetics of this reaction limits its practical application, because the proposed electrocatalysts still suffer from low activity and reduced stability [9].

CO₂ER follows a multi-electron pathway, mainly two-, four-, six-, eight-, twelve-electrons reduction steps, being these routes more favorable with respect to the single electron reduction of CO₂ to CO₂⁻, characterized by a very high thermodynamic potential [54]. According to this, different products can be obtained: carbon monoxide (CO, in gaseous form), formic acid (HCOOH, in liquid form) and oxalic acid ($H_2C_2O_4$, in liquid form); formaldehyde (CH_2O, liquid); methanol (CH_3OH, liquid); methane (CH_4, gas); ethylene (CH_2CH_2, gas) and

ethanol (CH_3CH_2OH, liquid); but also long carbon-chain hydrocarbons and alcohols. Equations (2)–(9) present the electrochemical reduction reactions associated to the listed products, together with the corresponding electrode potentials (V vs standard hydrogen electrode, SHE) measured in aqueous solutions under standard conditions (pH = 7, 1 atm and 25 °C) [55].

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + 2H_2O \ (-0.106\,\text{V}) \tag{2}$$

$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH \ (-0.250\,\text{V}) \tag{3}$$

$$2CO_2 + 2H^+ + 2e^- \rightarrow H_2C_2O_4 \ (-0.500\,\text{V}) \tag{4}$$

$$CO_2 + 4H^+ + 4e^- \rightarrow CH_2O + H_2O \ (-0.070\,\text{V}) \tag{5}$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \ (0.016\,\text{V}) \tag{6}$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \ (0.169\,\text{V}) \tag{7}$$

$$2CO_2 + 12H^+ + 12e^- \rightarrow CH_2CH_2 + 4H_2O \ (0.064\,\text{V}) \tag{8}$$

$$2CO_2 + 12H^+ + 12e^- \rightarrow CH_3CH_2OH + 3H_2O \ (0.084\,\text{V}) \tag{9}$$

It has to be highlighted that the potentials here reported for the different reactions are representative only from the thermodynamic point of view, but do not give any information on the kinetics, in terms of reaction rates and mechanisms involved, which can be quite different in the diverse cases. In addition, it should be clarified that quite often there is not a single reduction product: a mixture of two or more species (both liquids and gases) can be the result of a single reduction process [10]. For this reason, the selectivity of the product is another most important parameter to take into account when proposing novel catalysts. Indeed, as will be clarified down below, the number and the type of the product species is largely dependent on the applied potential, and the correct choice of the operational parameters could permit to obtain a specific product with a high conversion efficiency.

In Fig. 1 a typical cyclic voltammetry curve for the electrochemical reduction of CO₂ in aqueous electrolytic solution is presented, together with a curve related to the same catalyst acquired in a nitrogen-saturated solution. The CO₂-related curve is characterized by a constant quasi-null current density at larger potentials, followed by an increasing cathodic current starting from the onset potential and going toward negative values. Similar behavior can be observed in the voltammogram measured in N₂-saturated solution: in this case, in the very low-potential region (0 V vs SHE), the hydrogen evolution reaction (HER) takes place. Unfortunately, HER proceeds also in CO₂-saturated electrolytes, thus competing with the CO₂RR, by subtracting the electrons
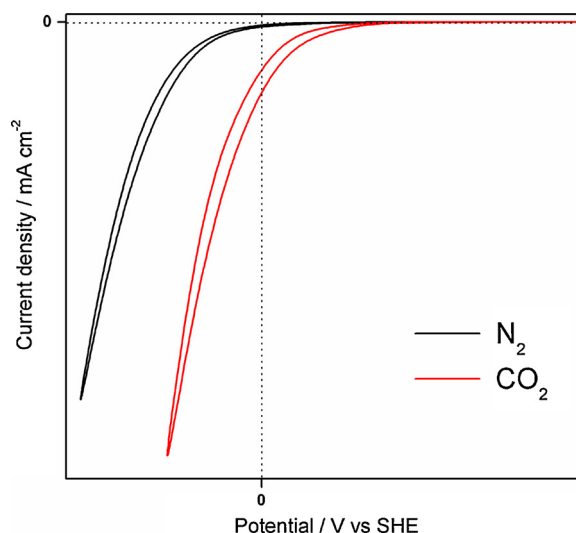

Fig. 1. Typical cyclic voltammetry curves of a CO₂RR catalyst in N₂- and CO₂-saturated aqueous electrolytic solutions.