Electrochemical impedance spectroscopy: Fundamentals and application in dye-sensitized solar cells

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ABSTRACT

Dye-sensitized solar cells (DSCs) have emerged in the photovoltaic scenario as one of the most promising low-cost alternative to the most employed solar devices based on silicon, especially for some niche application. Despite of the huge work carried out by scientists and researchers, detailed mechanism of some of the charge transfer processes occurring inside DSCs is not still fully understood. Electrochemical impedance spectroscopy (EIS) gave an immense help in analyzing these processes, and has been widely employed in the DSCs to characterize novel materials and architectures. The scope of this Review is to provide an insight on the application of EIS for the study of DSCs. A general introduction of the technique will be given, followed by an in-depth review of its application in the DSC field. Finally, a brief discussion of future research directions concerning this topic will be presented.

1. Introduction

In the last decades, the increasing demand for greener and sustainable energy production drove the scientific community to develop innovative systems able to convert solar [1], wind [2] or chemical [3] energy into electricity. Among all the available renewable sources, surely photovoltaic (PV) represents one of the most promising, being characterized by reduced maintenance costs, low noise during operation, and the possibility to be locally exploited. In addition, similarly to other renewable sources, its use can reduce the global CO_2 emission. Also looking from an energetic point of view, PV embodies a sustainable and winning strategy: in fact, energy coming yearly from the Sun represents about 10,000 times the current global energy consumption [4], and this implies that if only 0.1% of the our planet surface (which roughly corresponds to 1% of desert areas) were covered with 10% efficiency solar cells, our present needs of energy would be satisfied [5].

The entire PV scenario is currently divided in three different technologies, called "generations". The "first generation" is mainly constituted by mono- and poly-crystalline bulk silicon devices, and it is characterized by relatively low costs (about 1.2 €/W) and high efficiencies (larger than 20%). However, a known issue of these cells is their reduced capability of absorb the diffuse component of the light radiation. This limitation is not present in the "second generation" devices, which are fabricated with amorphous thin films (silicon, cadmium telluride, copper indium gallium selenide, among others), characterized by larger absorption coefficients if compared to crystal-

line materials. The manufacturing costs are usually lower with respect to first generation devices (with comparable efficiencies), but the used materials are often toxic and in some cases exhibiting reduced long-term stability. The principal characteristic of the "third generation" solar cells is the extremely low fabrication cost, thanks to the use of exceptionally cheap raw materials: nanostructured semiconductor layers in the case of dye-sensitized solar cells, or polymers for what concerns the organic solar cells [1].

Dye-sensitized solar cells (DSCs) are composed by three main elements: a photoanode, a ionic conducting medium and a counter electrode (cathode). The first one is constituted by a porous semiconductor (usually TiO_2 nanoparticles) deposited on a transparent conductive oxide (TCO)-covered glass and sensitized by dye molecules, which absorb the incoming light, generate electrons and transfer them to the front electrode. The regeneration of dye molecules is obtained through a redox couple (usually dissolved in an organic solvent). A Pt thin film deposited on another TCO-covered glass represents the counter electrode, whose main purpose is to speed up the electrolyte reduction reaction. As anticipated above, these cells exhibit numerous advantages, namely relatively high efficiencies (about 12%) [6] and low manufacturing costs (with a prevision to achieve 0.3 €/W). In addition they present some peculiar features, like their transparency or their possibility of assuming different colors (by exploiting different dyes), thus being used as Building-Integrated Photovoltaics (BIPV). Global DSC market was valued at about 50 M$ in 2014 and it is estimated to increase up to 130 M$ in 2022. Currently the most widespread areas of application are BIPV and portable charging (mainly in Europe and
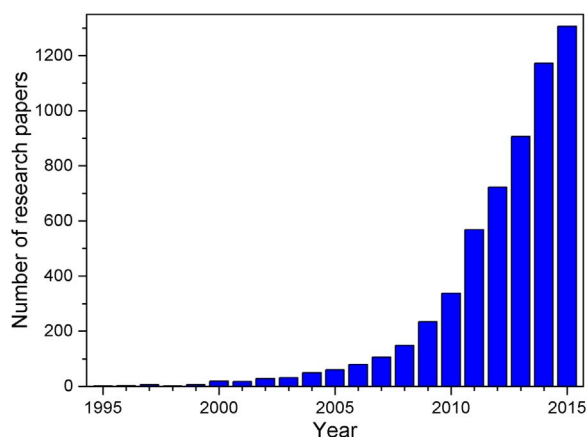
Fig. 1. Numbers of research articles published per year in the period 1995–2015 obtained from a simple and limited literature search using the keywords "Dye-sensitized Solar Cells" and "Electrochemical Impedance Spectroscopy" (source Scopus).

North America), but in the next years a great increment is expected in other sectors such as embedded electronics, automotive and outdoor advertising, with a decisive boost in countries like China and India [7]. The DSCs were invented in 1991 by O'Regan and Grätzel [8]. Starting from that seminal paper, a lot of research has been carried out on these devices. Novel materials have been proposed for photoanodes [9–12], sensitizers [13–18], counter electrodes [19–22] and redox couples/hole conducting media [9,23–26]. Moreover a lot of effort has been focused on the comprehension of all the mechanisms involved during the operation of DSCs [27–34]. However, not all of them are currently comprised in detail, like the electron injection process or the charge transport through the mesoporous layer [9] (a description of these mechanisms will be reported in Section 3).

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 occurring inside these devices [35–41], as well as for the characterization of cell materials and components [42–47]. This is witnessed by the huge and increasing number of publications regarding this topic in the last twenty years (see Fig. 1), which represents about the 10% of the total number of research papers concerning DSCs.

The above reported considerations justify the needing for a comprehensive collection of the most important results obtained in this field. Thus, in this article, the application of Impedance Spectroscopy in DSC studies is reviewed. The aim of this review is both to provide a starting point to researchers who begin embarking in the field of EIS and to give to scientists working on DSCs an overlook on the possibilities of application of this technique for the study of these devices. Accordingly, the paper is subdivided as follows: Section 2 briefly presents the fundamentals of EIS technique, together with some example of simple equivalent circuits used to model the system under study; Section 3 reports on the DSC working principle, with a particular focus on the charge transfer processes; Section 4 is devoted to the application of EIS in the study of the various mechanisms, with emphasis on the different components of the DSCs; Section 5 provides a general conclusion on the basis of the previous sections, together with a brief discussion of future research directions for EIS in DSC field.

2. Electrochemical impedance spectroscopy

2.1. Fundamentals

Impedance spectroscopy (IS) is mainly divided into two categories: electrochemical IS and dielectric IS. The principal difference lies into the material, device, or system under study: as suggested by the name, the latter involves the analysis of dielectric materials, with predomi-

nant electronic conduction; on the other hand, EIS applies on materials in which the ionic conduction is prevalent on the electronic one [48]. Examples of such systems are solid and liquid electrolytes [49–51], glasses [52–54] and polymers [55–57], but this technique has been largely employed also in the study of corrosion [58,59] or electrochemical and photoelectrochemical cells, such as fuel cells [60–62], batteries [63–65], or solar devices [66,67].

EIS is based on the application of an AC voltage (or current, in the case of galvanostatic EIS) to the system under study and on the analysis of the AC current (voltage) response as a function of the frequency. It is usually carried out through the use of a potentiostat and a frequency response analyzer (FRA), and it can be performed in 2- or 3-electrodes configuration, depending on the absence (2-electrodes) or the presence (3-electrodes) of a reference electrode, whose potential is known and fixed [68]. A constant DC voltage may be superimposed to the AC signal; the amplitude of the latter should be as low as possible (*small signal* approximation) in order to consider the system under study as pseudo-linear. In fact, usually the electrochemical systems are intrinsically not linear, but under small signal conditions the measurement can be confined in a pseudo-linear region of the current-voltage curve of the system; typical values lie in the range of some tenths of mV [69]. The frequency may span over a wide range, usually from some MHz down to few mHz.

During the EIS measurements, the small signal sinusoidal voltage $V(\omega,t)=V_o\sin\omega t$ with amplitude V_o and variable frequency f ($f=\omega/2\pi$, where ω is the angular frequency) is applied to the system under study, and the response current $I(\omega,t)$ is measured at the same frequencies. The impedance $Z(\omega,t)$ related to the system can be calculated through the Ohm's law as:

$$Z(\omega, t) = \frac{V(\omega, t)}{I(\omega, t)} \tag{1}$$

For a given ω, the current response could be *in-phase* or *out-of-phase* with respect to the voltage stimulus, so that its general expression is given by $I(\omega,t)=I_o\sin(\omega t-\theta)$ [68], where I_o is the current signal amplitude and θ is the phase angle between voltage and current. By exploiting the complex number notation, the AC voltage and current signals can be expressed as $V(\omega,t)=V_o e^{j\omega t}$ and $I(\omega,t)=I_o e^{j(\omega t-\theta)}$ respectively, where j is the imaginary unit. With these notations, Eq. (1) can be rewritten as:

$$Z(\omega, t) = \frac{V(\omega, t)}{I(\omega, t)} = \frac{V_0}{I_0}e^{j\theta} = |Z(\omega)|e^{j\theta} \tag{2}$$

where $|Z|$ is the impedance modulus and θ is the impedance phase. Eq. (2) can be further modified by applying Euler's relationship, thus obtaining:

$$Z(\omega, t) = |Z(\omega)|(\cos\theta+j\sin\theta) = Z'(\omega)+jZ''(\omega) \tag{3}$$

where $Z'=|Z|\cos\theta$ and $Z''=|Z|\sin\theta$ are the real and the imaginary part of the impedance, respectively. From Eq. (3), the modulus and the phase of the impedance can be obtained from:

$$|Z(\omega)| = \sqrt{Z'^2(\omega) + Z''^2(\omega)} \tag{4}$$

$$\theta(\omega) = \tan^{-1}\left(\frac{Z''(\omega)}{Z'(\omega)}\right) \tag{5}$$

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. Even if not always observed in the published literature, it is good practice to employ isometric axes in this type of graph: this is particular useful in order to immediately detect the possible presence of non-ideal capacitive behavior, as described below (Section 2.3). The Nyquist representation is more compact than the following, even if the frequency dependence is not explicitly evident. On the other part, the Bode plots are a pair of graphs reporting $\log|Z|$ and θ as a function of $\log f$ (less used representations report Z' and Z'' as a function of $\log f$) [48].