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# Exact analytical analysis of current density-voltage curves of dye-sensitized solar cells

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#### Abstract

In this work, a simple and a straight-forward approach to derive the parameters of dye-sensitized solar cells (DSSCs) in terms of single diode model is discussed. The parameters are extracted exclusively from single current density–voltage (j-V) curve with some common assumptions. The technique does not require smoothing of the j-V curve by means of polynomial fitting as well as iterative calculation of the diode model equation. The data obtained from this method are compared with that obtained from least square fitting and the combined analyses of electrochemical impedance spectroscopy (EIS) and j-V data for two different DSSCs. The method is suitable for routine analysis of DSSCs.

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## 1. Introduction

Dye-sensitized solar cells (DSSCs) have become an active field of research due to their attractive properties: low cost, colorful, transparent, flexible and operational under diffuse light.(Gao et al., 2008; Hardin et al., 2012) A typical DSSC composed of a ruthenium dye loaded TiO<sub>2</sub> photoelectrode (PE), a redox electrolyte based on  $I^-/I_3^-$  and a platinized counter electrode (CE) showed efficiency up to 11.3% (Gao et al., 2008; Meyer, 2010; Nazeeruddin et al., 2005); and a DSSC with porphyrin dye and cobalt based redox electrolyte reached efficiency as high as 12.3% (Yella et al., 2011). Moreover, the recent report on the record efficiency of 15% for a perovskite

http://dx.doi.org/10.1016/j.solener.2015.03.009 0038-092X/© 2015 Elsevier Ltd. All rights reserved. sensitized solar cells (Burschka et al., 2013) has accelerated the research activities on this technology. Despite the record efficiency, it is essential to scale up the DSSCs from small laboratory sized unit cells to large modules with new materials and methods that ensure lower price, longer operating lifetime and higher efficiency. In this regard, understanding the key parameters influencing photovoltaic performance of the devices is essential.

The relation between external cell current density  $(j_{cell})$  and voltage  $(V_{cell})$  for DSSCs can be expressed by the following diode model equation (Barea et al., 2010b; Halme et al., 2010; Sarker et al., 2014)

$$j_{\text{cell}} = j_{\text{ph}} - j_0 \left[ \exp\left\{ \frac{-q(V_{\text{cell}} - j_{\text{cell}}R_{\text{s}})}{mk_{\text{B}}T} \right\} - 1 \right] + \frac{V_{\text{cell}} - j_{\text{cell}}R_{\text{s}}}{R_{\text{sh}}}$$
(1)

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where  $j_{ph}$  is the photogenerated current density,  $j_0$  the dark saturation current density, m the ideality factor,  $R_s$  the series resistance,  $R_{\rm sh}$  the shunt resistance,  $k_{\rm B}$  the Boltzmann's constant, q the elementary charge, and T the absolute temperature. In DSSCs, the ideality factor m was recognized as the inverse of the transfer factor  $\beta$  (Barea et al., 2010b; Bisquert and Mora-Sero, 2010; Sarker et al., 2014). Also, note that Eq. (1) follows the sign convention that  $V_{\text{cell}} < 0$  and  $j_{\text{cell}} > 0$  in the potential range of 0 to open-circuit voltage ( $V_{oc}$ ). Even though Eq. (1) is only valid for DSSCs that show typical current density-voltage (j-V)curves, (Barea et al., 2010b; Fabregat-Santiago et al., 2007; Sarker et al., 2014) calculating j-V curves through the equation is a powerful approach to factor out the parameters that limit the device performance because the photovoltaic properties of the devices can be explained with a few parameters. The parameters can be obtained from combined analyses of i-V and electrochemical impedance spectroscopy (EIS) data (Barea et al., 2010b; Sarker et al., 2014). Another way to extract the parameters is to fit the experimental j-V curve to Eq. (1), (Jain and Kapoor, 2004; Zhang et al., 2011) which is implicit in nature and cannot be solved analytically for either  $j_{cell}$  or  $V_{cell}$ . Thus, an explicit expression of Eq. (1) with Lambert W function is used to fit the experimental j-V curves (Zhang et al., 2011).

$$j_{cell} = \frac{R_{sh}(j_{ph} + j_0) - V_{cell}}{(R_{sh} + R_s)} - \frac{mk_B T}{qR_s} Lambert W \left[ \frac{qR_s j_0 R_{sh} \exp\left\{\frac{qR_{sh} R_s(j_{ph} + j_0) + R_{sh} V_{cell}}{mk_B T(R_{sh} + R_s)}\right\}}{mk_B T(R_{sh} + R_s)} \right]$$
(2)

where LambertW is the Lambert W function that can be solved numerically. The parameters obtained by fitting an experimental j-V curve to Eq. (2) are strongly influenced by their initial guess (Halme et al., 2010; Tian et al., 2011). As a result, fitting to the explicit expression without proper initial guess may lead to wrong cell parameters most of which may not have any physical meaning. To overcome this situation, different techniques based on either theoretical models or graphical treatments were proposed to extract the cell parameters with reasonable physical significance (Cotfas et al., 2013; Das, 2012). However, those methods are rather complicated. On the other hand, the combined analyses require a set of EIS spectra measured at steady-states corresponding to different potentials between open-circuit and short-circuit of the DSSC under investigation (Barea et al., 2010b; Sarker et al., 2014). Generally, one set of EIS measurement takes more than an hour for a single cell. As a result, it becomes very difficult to maintain the steady-state of the cell throughout the measurement as the cell temperature may change with time due to continuous illumination for long time. Moreover, analysis of the set of EIS data involves intricate processes such as fitting to an appropriate equivalent circuit impedance model followed by extracting meaningful value of the equivalent circuit elements. Thus, it is desirable to find a faster and easier method to extract the parameters.

Here, we demonstrate a new method for extracting the cell parameters such as  $j_{ph}$ ,  $j_0$ , m,  $R_s$ , and  $R_{sh}$  solely from the analysis of a single j-V data and applied the method to characterize DSSCs composed of two different liquid electrolytes. In this method, the cell parameters are extracted mainly from the total differential resistance of experimental j-V curves. The method does not require any iterative calculation or smoothing of the experimental data by means of polynomial fitting. Finally, the data obtained from the analysis are compared to that obtained from fitting and combined analyses of EIS and j-V data.

#### 2. Theory

### 2.1. Equivalent circuit, total resistance, and j-V curve

The equivalent circuit corresponding to Eq. (1) is shown in Fig. 1 where the parallel combination of the shunt resistance  $(R_{\rm sh})$  and the recombination resistance  $(R_{\rm r})$  accounts for the loss of photogenerated current  $(j_{\rm ph})$ , and the series resistance  $(R_{\rm s})$  accounts for the loss of photogenerated voltage  $(V_{\rm PE})$  as  $V_{\rm cell} = V_{\rm PE} + j_{\rm cell}R_{\rm s}$ . According to the equivalent circuit of Fig. 1, total resistance  $(R_{\rm total})$  of DSSCs can be written as

$$R_{\text{total}} = R_{\text{s}} + \frac{R_{\text{r}}R_{\text{sh}}}{R_{\text{r}} + R_{\text{sh}}}$$
(3)

On the other hand,  $R_{\text{total}}$  can be derived from the derivative of the *j*-V data as (Fabregat-Santiago et al., 2007)

$$R_{\text{total}} = \left(\frac{dj_{\text{cell}}}{dV_{\text{cell}}}\right)^{-1} \tag{4}$$

Inversely, the j-V curve of the corresponding cell can be constructed from  $R_{\text{total}}$  using the short-circuit current density ( $j_{sc}$ ) through Eq. (5) (Fabregat-Santiago et al., 2007)

$$j_{\text{cell}} = j_{\text{sc}} - \int_0^{V_{\text{cell}}} \frac{1}{R_{\text{total}}} dV_{\text{cell}}$$
(5)



Fig. 1. Equivalent circuit diode model of dye-sensitized solar cells.

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