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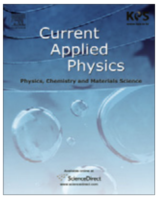

Optical and electrical modelling and characterization of dye-sensitized solar cells

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ABSTRACT

A route of optical and electrical modeling of dye-sensitized solar cells (DSSCs) has been developed and validated within a set of test structures. The optical model is based on one-dimensional semi-coherent optical simulator Sun*Shine*, in which nanoporous active layer was successfully modelled as effective medium layer with effective scattering of light at its front and back surface interface using effective roughness. The electrical model is based on a pseudo-homogeneous active layer using drift–diffusion transport equations for free electron and ion transport. In both models, input parameters have been extracted from measured performance of test devices and main optical and electrical losses have been quantitatively identified for ionic liquid based DSSC structures, having 7 or 14 μm thick active layer.

1. Introduction

Inexpensive manufacturing technology placed dye-sensitized solar cells (DSSCs) as a promising photovoltaic energy source and generated extensive R&D efforts since their invention [1]. Their structure and principle of operation differ significantly compared to conventional inorganic solar cells. To further enhance the record efficiencies, profound understanding of internal processes and parameters within these structure is necessary. Simulation tools offer a short cut in this endeavor, but accurate optical and electrical model are indispensable and need to be developed. A few different optical and electrical models of dye-sensitized solar cells have already proved their usefulness [2–9]. In this paper, a coupled optical and electrical model of dye-sensitized solar cell will be presented. Their input parameters will be determined through simplified structures and the simulation results will be verified on DSSCs based on binary ionic liquid electrolyte having single and double thickness of the active layer. Optical and electrical losses in the dye-sensitized solar cells will be discussed.

2. Experimental

An ionic liquid based dye-sensitized solar cells have been produced by our standard procedure. To fabricate active layer of DSSC three or fourfold layer deposition of TiO_2 is usually needed resulting in different layers *i.e.* transparent, active, scattering or reflective layer. In our case we use a novel paste formulation developed by applying the Pechini type sol–gel method [10] which allows realization of highly efficient photoactive layer by single deposition of TiO_2 paste. The first step in the preparation of the TiO_2 paste was the synthesis of a polyester-based titanium sol using a precursor molar ratio of 1:8:32 [titanium isopropoxide:citric acid:ethylene glycol]. The sol was prepared by heating ethylene glycol (Riedel-de Haen) to 60 °C and during stirring the titanium isopropoxide (Fluka) was added. Finally, the corresponding amount of citric acid (Fluka) was added and the temperature increased to 90 °C. The solution was stirred at this temperature until it turned clear. The paste was prepared by mixing the TiO_2 powder (P25, Degussa) and sol in a mortar grinder (Retsch, RM200) for 3 h. The molar ratio between the TiO_2 powder and titanium isopropoxide in the paste formulation was 7:1.

All pastes were deposited on a transparent conductive electrode (TCO) *i.e.* fluorine-doped SnO_2 on glass substrate, using the "*doctor blade*" technique. Layers were annealed at 450 °C for 1 h.

The TiO_2 layers with thicknesses 7 and 14 μm were immersed in an ethanol solution of the Ruthenium complex dye (Ru(2,2′bipyridyl-4,4′dicarboxylate)2 $(NCS)_2$, Solaronix) for 12 h. The dye loading was 1.24×10^{-4} mol/cm^3 [10]. For a counter electrode, platinum (thickness ~5 nm) was sputtered onto a TCO glass. Both electrodes were sealed with a 25 μm thick polymer foil (Surlyn, DuPont) that acts also as a 22 μm spacer (after sealing) between the electrodes. After sealing, the electrolyte was injected through two holes pre-drilled into the counter electrode. The electrolyte used was a binary ionic liquid mixture of 1-propyl-3-methyl-imidazolium iodide (Merck, $\rho = 1.55$ g/ml, $M = 252.1$ g/mol) and 1-ethyl-3-methyl-imidazolium tetracyanoborate (Merck, $\rho =$ g/ml, $M = 226.05$ g/mol) mixed in volume ratio 13:7, 0.2 M iodine (Merck), 0.5 M 1-methylbenzimidazole (Aldrich) and 0.1 M guanidine thiocyanate (Fluka). The resulting iodide and tri-iodide concentration were 3.80 M and 0.2 M, respectively. For each TiO_2

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thickness, three identical samples of DSSCs each with an active area of 0.5 cm^2 were assembled. Before characterization, the cells were stored in the dark at open circuit conditions for 24 h to allow the electrolyte to penetrate the TiO_2 pores.

All optical measurements (transmittance and reflectance) of individual layers or complete DSSCs were done with Lambda 950 Perkin Elmer spectrophotometer. The measurements were scanned in decrements of 5 nm from 1500 to 300 nm, while the light was collected with 150 mm Ulbricht integration sphere coated with Spectralon. Performance of DSSCs was determined under standard test conditions (STC) [11]. To set the cell temperature to 25 °C, the temperature was stabilized with a cooling/heating setup based on Peltier element designed for solar cell characterization. Oriel Class A solar simulator equipped with 1.5G Air mass filter was used as the light source and current–voltage characteristics (*I*–*V*) were measured using a Keithley 238 source meter by applying voltage and measuring current. The *I*–*V* measurements were scanned from 0 V (short-circuit condition) to 0.9 V (beyond open-circuit voltage), with 10 mV steps. We calculated the short-circuit current mismatch parameter and in conjunction with a calibrated c-Si reference solar cell covered with KG5 filter that resembles the spectral selectivity of DSSCs, we determined the level of standard (1 sun, 100 mW/cm^2) irradiance. During irradiance and characterization, the cells were covered with a black mask surrounding the active area of the cell. The spectral response of the assembled DSSCs was measured without bias light using Xenon lamp and a monochromator in wavelengths increments of 5 nm from 300 to 800 nm. In order to obtain stable signal reading, a 3 s delay was always applied between setting a wavelength and measurement of the current.

3. Results and discussion

For optical simulation and analysis of dye-sensitized solar cells, we used a one-dimensional semi-coherent optical simulator Sun*Shine* [12]. In the numerical simulator, direct (*i.e.* specular, non-scattered) light is analyzed in terms of coherent electromagnetic waves, whereas for scattered light at rough interfaces ray tracing technique is applied. Reflection and transmission properties of each interface and light scattering at each rough interface in the structure are considered in the simulations. Main input parameters of the simulator are: thicknesses of the layers, wavelength-dependent complex refractive indices of individual layers, while the scattering of light at the interfaces inside the structure is described with haze parameters, *H*, which describe how much of the incident light is scattered at an interface in reflection or in transmission, and the angular distribution function, *ADF*, which describes the directional dependency of scattered light. In accordance with the upgraded scalar scattering theory [13], the haze parameters are modelled with the root-mean-square roughness, σ_{rms}, arising from nanometer scale vertical roughness. The main output parameters of the simulator are reflectance and transmittance at each interface, absorptance in individual layers and generation rate profile across the structure, $G_L(\lambda,x)$, which is the main input parameter for an electrical model.

3.1. Optical model and input parameters

DSSC cells under investigation consist of the glass/TCO/active layer (TiO_2 + dye + electrolyte)/electrolyte/(Pt + electrolyte)/TCO/glass structure. Thickness of individual layers and their roughness are shown in inset of Fig. 2. To set up the optical model of a DSSC cell, its individual layers need to be optically characterized first [14,15]. The complex refractive index, $N(\lambda) = n(\lambda) - i\,k(\lambda)$, of glass (Elka microscope glass, 1 mm thick) and the commercial glass/TCO substrate (Asahi U-type SnO_2:F with thickness of 3.2 mm/600 nm and sheet resistivity of 10 Ω/□) have been determined from reflectance and transmittance measurements in the past. The electrolyte and active layer (mixture of TiO_2, dye and electrolyte) as device specific layers have to be characterized for each type of DSSC device separately.

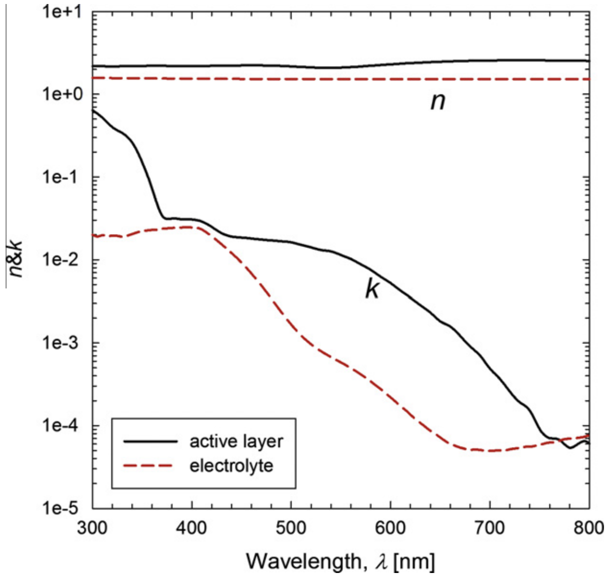

Fig. 1. Real part of complex refractive index (n) and extinction coefficient (k) for the active layer (black solid curves) and the electrolyte (red dashed curves).

First, the wavelength-dependent complex refractive index of electrolyte, $N_{el}(\lambda)$, was determined from total reflectance (R) and transmittance (T) measurements of a simplified stack: glass(1 mm)/electrolyte(22 μm)/glass(1 mm). Due to relatively thick layer of electrolyte the incoherent propagation of light was assumed in the model for determination of $N_{el}(\lambda)$. The real and imaginary part of $N_{el}(\lambda)$ is shown in Fig. 1 (red[1] dashed curves).

In the next step, the complex refractive index of nanoporous active layer of DSSC, $N_{act}(\lambda)$, was determined from $R(\lambda)$ and $T(\lambda)$ measurements. However, in this case a more complex structure was used for the determination of $N_{act}(\lambda)$: glass (1 mm)/active layer (7 μm)/electrolyte (15 μm)/glass (1 mm), since the presence of electrolyte in the active layer can be achieved by sealing the whole test structure between two glass plates. In all layers incoherent propagation of light was assumed. Due to relatively high energy band gap of TiO_2 (3.2 eV) the TiO_2 nanocrystals were assumed not to absorb the photons with sub-bandgap energies, but to act as good light scattering centers. In the optical model, inhomogeneous nanoporous active layer made of TiO_2 nanocrystals covered with dye and filled in with electrolyte was assumed as a homogenous effective medium layer, where the scattering inside the structure (from TiO_2 nanocrystals) could not be taken into account and thus, it was transformed to the scattering at the glass/active layer and the active layer/electrolyte interfaces by introducing effective σ_{rms} in accordance with scalar scattering theory [13]. The σ_{rms} was determined from fitting of simulated and measured wavelength-dependent haze function in reflectance. In case of 7 μm thick active layer, the σ_{rms} is 100 μm, while with thicker layers it increases. The *ADF* was determined with the angular resolved scattering system [14,15], which showed the elliptical angular dependence of scat-

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[1] For interpretation of color in Figs. 1–5, the reader is referred to the web version of this article.