Optical properties of iodine-based electrolyte used in bifacial dye-sensitized solar cells

Sameh O. Abdellatif

Received: 18 February 2022 / Accepted: 15 August 2022 / Published online: 15 September 2022
© The Author(s) 2022

Abstract
As third-generation solar cells, dye-sensitized solar cells (DSSCs) can show bifacial harvesting capabilities by utilizing transparent conducting oxides as a counter electrode. Herein, the electrolyte is considered a critical layer from the optical perspective. In this paper, an attempt to estimate the optical properties of Iodine-based electrolytes, typically used in dye-sensitized solar cells, is demonstrated. The refractive index for electrolyte as an effective medium is calculated to be $1.4535 \pm 0.005$ for an effective thin film of $33.4 \pm 0.5 \ \mu \text{m}$ thickness, using the near-infrared Fabry–Perot resonances. The extinction (absorption and scattering) and dispersion spectra for the prepared electrolyte were fitted using Lorentz–Dude (LD) model. Finally, the utility of the extracted optical parameters was examined through a finite difference time domain solver, Massachusetts Institute for Technology Electromagnetic Equation Propagation. The simulated optical transmission spectrum perfectly agreed with the measured spectrum with less than 0.1% root–mean–square error. The demonstrated attempt to accurately estimate the refractive index of electrolyte used in DSSCs fabrication may impacted theoreticians who are interested with the optoelectronic modelling of such electrochemical cells, as well as those dealing with optoelectronic devices informatics.

Keywords UV–vis spectra · FDTD Maxwell equation solver · Optical scattering · Refractive index · Electrolyte · Bifacial solar cells

1 Introduction
Photovoltaics operate on the concept of charge separation at a junction interface either in homo-junction or heterojunction forms (Cai et al. 2012; Liu et al. 2020). In the first generations, solid-state junctions made of silicon dominated. This was due to the material availability and industrial experience gained from the semiconductor fabricators (Liu et al. 2020). Next generations utilized inorganic/organic junction devices, for example, nanocrystalline, nanoporous, and conducting polymers films (Green 2002). These offer potential in new market share
dealing with IoT applications, low light intensity harvesting, diffused light-harvesting, and bifacial solar cells (Hassan et al. 2021; Hatem et al. 2021). New photovoltaic technology can move entirely from the classical solid-state junction by substituting the contacting interface to the semiconductor by a liquid-based electrolyte, gel, or solid-based electrolyte. This results in what we can call a photo-electrochemical solar cell (Roza et al. 2015).

Dye-sensitized solar cells (DSSC) have recorded a booming increase in the power conversion efficiency of the photo-electrochemical solar cell due to well fabricated nanoporous TiO$_2$ thin-film electrodes with a large surface area capable of absorbing a large amount of the immersed dye (Hassan et al. 2021; Abdellatif et al. 2018a, b, 2020). In DSSCs, electrolytes play an essential role in constructing the nanoporous TiO$_2$-dye-electrolyte interface, capable of acting as a charge separation junction (Chowdhury et al. 2020). Various electrolyte recipes that can be integrated with DSSCs, including but not limited to $I^-/I_{3}^-$, $Br^-/Br_{2}^-$, $SCN^-/SCN_2^-$, and Co(II)/Co(III), have been demonstrated in the literature (Chowdhury et al. 2020; Su’ait et al. 2015). Studies have shown that the most effective electrolyte to be used in dye-sensitized solar cells is Iodine-based $I^-/I_{3}^-$ electrolyte (Chowdhury et al. 2020). However, some drawbacks have been reported: it corrodes the glass, semiconductor, and platinum over time (Chowdhury et al. 2020). Alternatively, Iodine-based electrolytes showed long-term stability chemically, thermally, and electrochemically (Turyanska et al. 2011).

Optically, more attention has been given to the properties of both the porous TiO$_2$ and the dyes rather than the electrolyte (Hassan et al. 2021; Abdellatif et al. 2018a, b, 2020). This is directly attributed to the significant impact of the mesoporous active layer with immersed dye on the absorption performance of the DSSC. On the other hand, electrolyte, associated with the counter electrode, has a relatively weak contribution to the cell optical performance. Alternatively, in bifacial DSSCs (Hassan et al. 2021), the optical properties of the electrolyte would directly influence the cell performance. A previous attempt in Sangiorgi and Sanson (2017) investigated the optical impact of electrolyte on bifacial DSSCs. The study highlighted the transparency level of various dopped electrolyte on the counter electrode of the cell. However, the in-depth analysis of the refractive index calculations of Iodine-based electrolytes is missing so far, where this work considers it a literature gap.

This paper provides an attempt to investigate the optical performance of the Iodine-based electrolyte, commonly used in DSSC fabrication. Refractive index, extinction spectrum, and effective thickness have been calculated using experimental measurements and seeded in a finite difference time domain (FDTD) numerical model. The numerical transmission spectrum has been simulated against the experimentally measured spectrum. Herein, the extraction of the refractive index of the effective electrolyte medium in DSSC would be of interest for a broad readership including theoreticians and experimentalist dealing with photovoltaics for bifacial applications as well as third generation of solar cells. The demonstrated study combines a useful experimental data with the discussion of the possibility to design bifacial sells and explore the optical performance of electrolyte layer. As an output, the extracted refractive index can be inputted various optoelectronic simulator to describe the optical behavior of electrolyte in DSSCs generally, with specific importance in bifacial cells, where light is also injected from the counter electrode.
2 Experimental work and characterization

Experimentally, 2.49 gm of Potassium Iodide (KI) powder, 0.24 gm of Iodine (I) powder, 20 mL of acetonitrile (CH₃CN) solution, and 5 mL of Ethylene Glycol (C₂H₆O₂) are added in a clean beaker. Then, a magnetic stirring for 30 min at 100 rpm with no heating is applied to form a homogenous mixture, as shown in Fig. 1. The electrolyte is stored in a dark place to prevent it from degradation. For the sake of optical characterization, a V-770 UV–Vis-NIR spectrophotometer is used, with a wavelength variation from 190 to 2700 nm. All measurements have been conducted while considering air as a reference.

3 Optical numerical model

Numerically, the electrolyte is simulated as an effective medium with effective permittivity given by Choy (2015):

\[
\varepsilon_{\text{eff}} = \varepsilon_m \frac{2\varepsilon_i (\varepsilon_i - \varepsilon_m) + \varepsilon_i + 2\varepsilon_m}{\varepsilon_i + 2\varepsilon_m - \delta_i (\varepsilon_i - \varepsilon_m)}
\]

where \(\varepsilon_{\text{eff}}\) is the effective dielectric constant, \(\varepsilon_m\) is the medium dielectric constant, while \(\varepsilon_i\) is the inclusion dielectric constant, and \(\delta_i\) is the volume fraction of the inclusion (Choy 2015). Herein, we consider the Iodine and the Ethylene Glycol as the inclusion and the medium, respectively. The optical properties for inclusion and medium were captured from Chance et al. (2010), Zhang et al. (2008).

Fig. 1  a Iodine-based electrolyte, b segmented-DSSC before inserting electrolyte, c segmented-DSSC with the electrolyte
To model the electrolyte’s dispersive and extinction spectra, fitting coefficients are needed. Herein, we utilize the Lorentz–Dude (LD) model as a compatible model with the FDTD algorithm used later in simulating optical transmission (Abdellatif et al. 2014, 2018a). The complex permittivity of the material using the LD model could be expressed by Abdellatif et al. (2014):

\[ \varepsilon(\omega) = \varepsilon_{\infty} + j \sum_n \frac{\sigma_n \omega_n^2}{\omega_n^2 - \omega^2 - i\omega \Gamma_n} \]  

where \( \varepsilon_{\infty} \) is the instantaneous dielectric response (DC), \( \Gamma_n \) and \( \omega_n \) is the LD coefficients and \( \sigma_n \) is a function of position specifying the strength of the nth resonance.

4 Results and discussions

Toward investigating the visual impact of an electrolyte effective layer, a set of samples were prepared (see Fig. 1b, c) by depositing an Iodine-based electrolyte on a pre-prepared quasi-dense TiO\(_2\) layer supported on a glass substrate (Segmented-DSSC). The quasi-dense TiO\(_2\) thin film was fabricated using the same procedure in Hassan et al. (2021). These samples are then characterized using a UV–Vis spectrometer, as shown in Fig. 2. UV–Vis-NIR spectrometer measurements were conducted by sandwiching the electrolyte between to FTO coated glass electrodes, cf. Fig. 1c.

To estimate the effective refractive index of the electrolyte, Fabry–Perot oscillations observed in the spectral transmission (T–\(\lambda\)) measurements were adopted. Such spectra show Fabry–Perot resonances due to reflections at the thin film boundaries. The oscillations that appear on the near-infra-red region (800–1800 nm) were used to determine the effective thickness and the refractive index of the electrolyte as an effective medium. Near infra-red resonances are promoted to ensure zero extinction spectrum. Measured transmission spectrum is investigated as a function of wave number (\(k\)), i.e., reciprocal wavelength.

Fig. 2 Experientially measured transmission spectra for an Iodine-based electrolyte layer above quasi-dense TiO\(_2\) on a glass substrate. Bare segmented DSSC with quasi-dense TiO\(_2\) on a glass substrate, along with glass substrate, 0% transmission, and 100% transmission samples, are measured for reference.
The positions of the interference extrema on the wavenumber scale have a linear dependence on the interference order due to the periodicity of the cosine function. Therefore, this dependence was fitted with a straight line for each angle of incidence. The slope of this line \( m \) delivers the thickness dependent part of the optical path difference \( \Delta_d = (2m)^{-1} \). It differs from the total path difference \( \Delta = \Delta_d + \lambda/2 \). The dependence of \( \Delta_d \) on the incidence angle \( \alpha \) for s-polarized light is given by \( \Delta_d = 2d \sqrt{n^2} \), where basic statistically linear fitting is used. As a result, the refractive index for the Iodine-based electrolyte was determined to be \( 1.4535 \pm 0.005 \), while the thickness was found to be \( 33.4 \pm 0.5 \) μm.

A stimulating effect at 570 nm is observed. Inspection of the transmittance curve of the quasi-dense layer alone shows that at this same wavelength, the quasi-dense layer’s optical thickness is one halfwave, i.e., the quasi-dense layer is “absenting” at this point. In other words, at this wavelength, the quasi-dense layer’s admittance is the same as that of the glass substrate. Since the electrolyte’s real refractive index is also close to that of glass when the quasi-dense layer is absent, there is not enough refractive-index contrast in the effective cavity to support Fabry–Perot resonance fringe amplitude tends to zero. This alternative explanation is also supported by the fact that the fringe amplitude is at a maximum around 1100 nm, which corresponds to where the quasi-dense layer’s optical thickness is a quarter-wave (and the quasi-dense layer’s admittance is therefore at a maximum).

Referring to Eq. (1). A theoretically calculated refractive index for the prepared electrolyte can be determined. Following the optical data extracted from Chance et al. (2010), Zhang et al. (2008), the theoretical refractive index was 1.46. This shows 0.5% deflection to the experimental refractive index calculated above. Accordingly, effective medium theory showed validity in estimating such electrolyte compositions, where various recipes can be applied for refractive index estimation.

To embed the dispersive and extensive response for the prepared electrolyte, the LD model mentioned in Eq. (2) was utilized. The fitting process was implemented using the experimental data in Chance et al. (2010), Zhang et al. (2008). As observed in Fig. 3, a relatively weak dispersive effect is recorded (Fig. 3a), mainly due to the Ethylene Glycol (C\(_2\)H\(_6\)O\(_2\)) component. Alternatively, the absorption (Fig. 3b), in other words, extinction, behavior showed double peaks toward reddish. This showed consistency with the observation in Fig. 1a, attributed to the Iodine existence. As illustrated in Eq. (2) and based on

![Fig. 3 Dispersion and extinction spectra for the prepared Iodine-based electrolyte using LD fitting coefficients. Simulations are made using the LD fitting parameters: \( \varepsilon_\infty = 2.13, \sigma_1 = 1.5451 \times 10^4, \omega_1 = 0.12115, \Gamma_1 = 0.025477, \sigma_2 = 8.74121, \omega_2 = 0.57791, \Gamma_2 = 3.36124, \sigma_3 = 0.641211, \omega_3 = 3.41789, \Gamma_3 = 2.7154, \sigma_4 = 0.09454, \omega_4 = 1.17955, \Gamma_4 = 0.78998, \sigma_5 = 0.047321, \omega_5 = 0.45328, \) and \( \Gamma_5 = 0.045872 \)](image-url)
the observation in Fig. 3a, the dispersive effect can be easily neglected, leading to a wavelength-independent real refractive index as calculated above. Additionally, by referring to the extinction spectrum in Fig. 3b, it can be validated that the extinction tends to zero by 1000 nm wavelength. Accordingly, the near-infrared Fabry–Perot resonances used to determine the refractive index in Fig. 2 are extinction-free resonances as indicated above.

As a next step, LD fitting was inputted to MEEP (an acronym for Massachusetts Institute for Technology Electromagnetic Equation Propagation). MEEP is an open-source FDTD solver for Maxwell’s equations (Rinnerbauer et al. 2012). The running time and the required RAM for MEEP simulations depend on the simulated volume. The required RAM is roughly 100 bytes per pixel/voxel and the running time is about ten ns per pixel per time step (Oskooi et al. 2010). The chosen simulated volume is 100 μm × 100 μm with a reasonable voxel size of 100 nm. Simulations were conducted on a computational unit of 2× Xeon Gold 6240 2.6G processor, with 36 cores and 24 MB Cache, each 32 GB RAM, supported by 2× 480 GB SSD HD. Applying the boundaries and the inputs mentioned above, the segmented DSSC fabricated and characterized in Fig. 2 is simulated in Fig. 4 agonist the measured spectrum. Fortunately, a perfect matching was observed while considering the extinction and the dispersion behavior of the medium using LD fitting coefficients; all coefficients are listed in Fig. 3 caption. An overall root–mean–square error below 0.1% was observed along the wavelength of interest.

5 Conclusion

In conclusion, this letter explores experimentally and theoretically the optical properties of Iodine-based electrolytes used in fabricating DSSCs. Experimental transmission spectra were investigated, taking into observation the positions of the Fabry–Perot resonances refractive index of 1.4535 ± 0.005 is reached, while the theoretical calculations showed 0.5% variation in respect. The electrolyte as an effective thin film recorded a thickness of 33.4 ± 0.5 μm. To integrate the dispersion and extinction behavior of the

![Fig. 4](image)

Fig. 4 Measurements against simulation transmission spectra for an Iodine-based electrolyte layer above quasi-dense TiO₂ on a glass substrate

© Springer
prepared electrolyte. LD fitting model was applied. The LD coefficients showed integral-
ity with the proposed FDTD MEEP model. An overall 0.1% root–mean–square error was
recorded between numerically simulated results and experimentally measured transmission
spectrum. Gaining the advantage of extracting an ultra-accurate refractive index for Iodine-
based electrolyte used in DSSC, provide the future applicability of optimized DSSC with
the aid of machine learning model under DSSC-informatics.

Acknowledgements The authors would like to acknowledge the support and contribution of the STDF in
this work. As part of the STDF Project entitled, “Mesostructured Based Solar Cells for Smart Building
Applications”, Project ID#33502.

Authors’ contribution A single author manuscript.

Funding Open access funding provided by The Science, Technology & Innovation Funding Authority
(STDF) in cooperation with The Egyptian Knowledge Bank (EKB). The author would like to acknowledge
the support and contribution of the STDF in this work. As part of the STDF Project ID#33502.

Data availability The data that support the findings of this study are available as following: https://www.
mathworks.com/matlabcentral/fileexchange/76474-dssc-optical-modelling. Any other data that support the
findings of this study are available from the corresponding author upon reasonable request.

Code availability Not applicable’ for that section.

Declarations

Conflict of interest The Author declares that there is no conflict of interest.

Ethics approval Not applicable’ for that section.

Consent to participate A single author manuscript.

Consent for publication Author accepts the publication rules applied by the journal.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License,
which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long
as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Com-
mons licence, and indicate if changes were made. The images or other third party material in this article
are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the
material. If material is not included in the article’s Creative Commons licence and your intended use is not
permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly
from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

References

Abdellatif, S., Ghannam, R., Khalil, A.S.G.: Simulating the dispersive behavior of semiconductors using the
Lorentzian–Drude model for photovoltaic devices. Appl. Opt. 53, 3294–3300 (2014). https://doi.org/10.1364/AO.53.003294
Abdellatif, S., Josten, S., Sharifi, P., et al.: Optical investigation of porous TiO2 in mesostructured solar
cells. In: Physics and Simulation of Optoelectronic Devices XXVI International Society for Optics and
Photonics (2018a)
Abdellatif, S., Sharifi, P., Kirah, K., et al.: Refractive index and scattering of porous TiO2 films. Micropo-
rous Mesoporous Mater. 264, 84–91 (2018b)
Abdellatif, S.O., Josten, S., Khalil, A.S., Erni, D., Marlow, F.: Transparency and diffused light efficiency
of dye-sensitized solar cells: tuning and a new figure of merit. IEEE J. Photovolt. 10, 522–530 (2020)
Cai, X., Wang, Y., Chen, B., et al.: Investigation of InGaN pin homojunction and heterojunction solar cells. IEEE Photonics Technol. Lett. 25, 59–62 (2012)

Chance, R., Shaw, M., Telgmann, L., Baxter, M., Carpenter, L.: A comparison of spectrophotometric and denuder based approaches for the determination of gaseous molecular iodine. Atmos. Meas. Tech. 3, 177–185 (2010)

Chowdhury, F.I., Buraidah, M., Arof, A., Mellander, B.-E., Noor, I.: Impact of tetrabutylammonium, iodide and triiodide ions conductivity in polyacrylonitrile based electrolyte on DSSC performance. Sol. Energy 196, 379–388 (2020)

Choy, T.C.: Effective Medium Theory: Principles and Applications. Oxford University Press (2015)

Green, M.A.: Third generation photovoltaics: solar cells for 2020 and beyond. Phys. E Low-dimens. Syst. Nanostruct. 14, 65–70 (2002)

Hassan, M.M., Ismail, Z.S., Hashem, E.M., Ghannam, R., Abdellatif, S.O.: Investigating the tradeoff between transparency and efficiency in semitransparent bifacial mesosuperstructured solar cells for millimeter-scale applications. IEEE J. Photovolt. (2021). https://doi.org/10.1109/JPHOTOV.2021.3086443

Hatem, T., Ismail, Z., Elmahgary, M.G., Ghannam, R., Ahmed, M.A., Abdellatif, S.O.: Optimization of organic meso-superstructured solar cells for underwater IoT® self-powered sensors. IEEE Trans. Electron Devices (2021). https://doi.org/10.1109/TED.2021.3101780

Liu, Y., Li, Y., Wu, Y., et al.: High-efficiency silicon heterojunction solar cells: materials, devices and applications. Mater. Sci. Eng. R. Rep. 142, 1–41 (2020)

Oskooi, A.F., Roundy, D., Ibanescu, M., Bermel, P., Joannopoulos, J.D., Johnson, S.G.: MEEP: A flexible free-software package for electromagnetic simulations by the FDTD method. Comput. Phys. Commun. 181, 687–702 (2010)

Roza, L., Rahman, M., Umar, A., Salleh, M.M.: Direct growth of oriented ZnO nanotubes by self-selective etching at lower temperature for photo-electrochemical (PEC) solar cell application. J. Alloys Compd. 618, 153–158 (2015)

Rinnerbauer, V., Ndao, S., Yeng, Y.X., et al.: Recent developments in high-temperature photonic crystals for energy conversion. Energy Environ. Sci. 5(10), 8815–8823 (2012)

Sangiorgi, N., Sanson, A.: Influence of electropolymerized polypyrrole optical properties on bifacial dye-sensitized solar cells. Polymer 125, 208–216 (2017)

Su’aït, M.S., Rahman, M.Y.A., Ahmad, A.: Review on polymer electrolyte in dye-sensitized solar cells (DSSCs). Solar Energy 115, 452–470 (2015)

Turyanska, L., Makarovsky, O., Elfurawi, U., Patanè, A., Fay, M.W., Bowers, J.W., Upadhyaya, H.M.: Imaging the photovoltaic response of PbS-sensitized porous titania. Phys. Status Solidi A 208, 2450–2453 (2011). https://doi.org/10.1002/pssa.201127066

Zhang, J., Zhang, P., Ma, K., Han, F., Chen, G., Wei, X.: Hydrogen bonding interactions between ethylene glycol and water: density, excess molar volume, and spectral study. Sci. China Ser. B: Chem. 51, 420–426 (2008)

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.