This work describes a modeling investigation of a working Dye-sensitized Solar Cells, including the contribution of ionic drift in the mass transport process of \( I_{\text{cell}} / I_{\text{redox}} \) couple. We found that the effective built-in electric field profile inside the cell is influenced by the density and distribution of the electronic traps located below the conduction band edge of the TiO\(_2\). Although the value of electric field remains low compared to conventional p-n junction solar cells, our results support that the high concentration of ionic species composing the electrolyte prompts a drift current of ionic species, comparable to the related ionic diffusion current, when the device is exposed to light illumination under short-circuit conditions. The simulations carried out for different electrolyte compositions tend to demonstrate that ionic drift is a process which can never been suppressed and therefore should be considered in the description of the mass transport. These results participate in the better understanding of the working principle of the complex and multifaceted chemistry of dye-sensitized solar cells.

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interface is assumed to be spatially homogeneous along the active layer thickness. This potential difference is lumped in the definition of the band edges of the effective medium. This approach has been widely used for inorganic semiconductors, Organic Solar Cells and Dye Solar Cells. The presence of a porous interface in DSC with solid electrolyte has been simulated considering the real interface in our previous work. We can claim that the effective model for a porous medium is a valid approximation when both materials involved are characterized by a high permittivity, which is the case of standard DSC. Therefore effects of microscopic electric fields in the cell such as electrochemical double layer formed at the interface between the TiO2/dye/electrolyte included between 0 and d is modeled as an effective medium, whereas the region between d and L is treated as bulk electrolyte.

The driving force for charged particles, namely the electrons in the TiO2 and ionic species in the electrolyte, is the gradient of their electrochemical potentials, which includes both the chemical potential for particle accumulation and the electric field induced by local charge density. The resolution of Poisson equation allows to calculate the electric field and the distribution of the electrostatic potential across the whole cell depth.

The constitutive equations are therefore coupled to the Poisson equation and solved in terms of electrochemical potential $\phi_y$:

$$\nabla \cdot j_y = \nabla \cdot (\mu_y n_y \nabla \phi_y) = \Lambda_y (G - R)$$

$$\nabla \cdot (\varepsilon \nabla \phi) = -q [n_e^+ + n_D^+ - n_I^- - n_e^-]$$

where $G$ and $R$ are the generation and recombination rate respectively, $\Lambda_y$ is the stoichiometric coefficient which is linked to the chemical reaction of the different species to recombination and generation, and its value is reported in Table I for different species. In Eq. 4, $q$ is the elementary charge and $\varepsilon$ the dielectric constant which is assumed to be homogeneous in the effective material and it is calculated following the Maxwell-Garnet approximation for mixed mesoporous media. $n_D^+$ represents the steady state concentration of ionized dyes in the cell, which is generally very low at standard light intensities, $n_e^-$ is the equilibrium concentration of electrons in the TiO2, equal to the intrinsic doping of the oxide, and $n_I^-$ the trapped electron density.

An important role in DSC is played by trapped electron density in TiO2. It has been demonstrated theoretically and through comparison with experimental data that electron trapping is not influencing the steady state electron transport, as long as trapped charges are not involved in the recombination process or supplying an additional pathway for transport via hopping mechanism. Therefore the effect of traps can be treated analytically in a pure diffusion model considering a distribution of localized states below the TiO2 conduction band edge, where trapped electrons are in equilibrium with those in the conduction band and can be released by thermal activation. This analytical approach (Multi Trapping Model, MTM) is valid as long as the electric field in the cell is negligible. In this paper we still assume that trapped states are not involved in transport. Concerning recombination, despite recombination via trapped state is possible, we assume that recombination between via trapped electrons is negligible respect to recombination via conduction band electrons and its contribution can be accounted by correcting the recombination rate by non-ideality factor in Eq. 7. The novelty consists in including into the model the key parameter of trapped states not in an effective way but inserting an exponential density of states below the conduction band edge of the TiO2:

$$n_I = \int_{E_c}^{\infty} N e^{-\beta \frac{E-E_c}{kT}} E dE$$

where $N_e$ is the effective density of trapped states and $\beta$ is describing the energy depth of the distribution under the conduction band edge ($E_c$), and $f_{FD}$ is the Fermi-Dirac distribution function. As in MTM, we assume that the conduction band and the trapped electrons are in thermodynamic equilibrium, meaning that the trapping-detrapping is faster than any other process. We will show that electron trapping can indeed influence the electrostatics of the device.

Photocurrent generation is accounted in the model with a Lambert-Beer approximation:

$$G(x) = \int_{0}^{\lambda_{max}} \Phi(\lambda) Q(\lambda) e^{-\alpha L_x} d\lambda$$

where $\Phi(\lambda)$ is the solar flux at wavelength $\lambda$, $Q(\lambda)$ is the quantum efficiency, $\alpha$ is the absorption coefficient and $L_x$ is the thickness of the active layer.

### Table I. List of parameters used to simulate a working DSC.

<table>
<thead>
<tr>
<th>Charged Species</th>
<th>Symbol γ</th>
<th>Recombination coefficient $\Lambda_y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>electrons</td>
<td>$e^-$</td>
<td>1</td>
</tr>
<tr>
<td>iodide</td>
<td>$I^-$</td>
<td>-1.5</td>
</tr>
<tr>
<td>tri-iodide</td>
<td>$I_3^-$</td>
<td>0.5</td>
</tr>
<tr>
<td>cation</td>
<td>$C^+$</td>
<td>0</td>
</tr>
</tbody>
</table>

*The electrochemical potential $\phi_y$ of a species $\gamma$ with charge $z_\gamma q$ is defined as:

$$\phi_y = \phi_0^\gamma + k_B T \ln \frac{n_{\gamma}^e}{n_{\gamma}^0} + z_\gamma q \phi$$

where $\phi$ is the inner electrostatic potential, $n_{\gamma}$ is the concentration of the species and $n_{\gamma}^0$ is the concentration of some reference state for which the chemical potential takes its standard value $\phi_0^\gamma$. 

---

Figure 1. Scheme of the cell. The electron collector is at the TCO/TiO2 interface, namely at $x = 0$. The counter-electrode is placed at Pt/TCO interface at $x = L$. The TiO2/dye/electrolyte included between 0 and d is modeled as an effective medium, whereas the region between d and L is treated as bulk electrolyte.
where \( \Phi(\lambda) \) is the AM1.5 solar spectrum, and \( \alpha(\lambda) \) is the dye absorption spectrum chemisorbed on the mesoporous medium, which can be extracted experimentally using a layer-by-layer spectroscopy measurement.\(^\text{32}\) Light absorption is assumed to occur by the charge transfer in the dye only. Absorption by direct interband excitation of TiO\(_2\) or the absorption of I\(_2\) in the blue spectral range are not considered.

The predominant recombination path in the cell takes place at the TiO\(_2\)/electrolyte interface involving the reduction of I\(_{-}\) by conduction band electrons in TiO\(_2\).\(^\text{33}\) This recombination rate (\( R \)) is given by

\[
R = k_r \left[ n^{3/2} \frac{n_{t_{1}}}{n_{t_{2}}} - n^{3} \frac{n_{t_{2}}^{3/2} n_{t_{1}}}{n_{t_{2}}^{3/2} n_{t_{1}}} \right]^{\beta_n}
\]

with \( k_r \) the recombination constant and \( \beta_n \) the relative dark densities for each species. The parameter \( \beta \) can be identified as the non ideality factor described in several works, which could account for the recombination with surface states.\(^\text{33}\)

Finally, for boundary conditions we use the following relations. No electrons from the TiO\(_2\) can be collected by the counter-electrode (the cathode), i.e. following the notation in Fig. 1 \( \nabla \Phi|_{x=0} = 0 \) and no ionic species can exchange charges with the anode collector, i.e. \( \nabla \Phi|_{x=\infty} = \nabla \Phi|_{x=\infty} = 0 \). The counter-ion does not contribute to the external current (\( \nabla \Phi|_{x=0, x=\infty} = 0 \) both at the electrode and counter-electrode). No charge accumulation occurs at the contacts (\( \nabla \Phi|_{x=0, x=\infty} = 0 \)).

The counter electrode is constituted by a thin layer of platinum nanoparticles deposited on the conductive glass. This layer acts as a catalyst to reduce the activation energy required for I-I bond breaking to reduce tri-iodide to iodide. The kinetic aspect of this charge transfer reaction is following the Butler-Volmer equation. The boundary conditions for iodide and tri-iodide ions are:

\[
J_{I^2} = -\frac{3}{2} J_0 [e^{\frac{\eta}{2}} - e^{-\frac{\eta}{2}}]
\]

\[
J_{I^3} = -\frac{1}{2} J_0 [e^{\frac{\eta}{2}} - e^{-\frac{\eta}{2}}].
\]

In the Equations 8 and 9, the current is distributed according to the stoichiometry of the redox reaction. \( \eta \) is the overvoltage at the cathode and \( J_0 \) the exchange current.

The last boundary condition concerns the carriers at the TCO interfaces with electrolyte and TiO\(_2\). An ideal contact shows very low recombination with surface states.\(^\text{31}\) Finally, for boundary conditions we use the following relations.

**Results and Discussion**

*Electrostatic influence of electron trapped states.*— Using the multiscale model described in the previous section, in this part we show the effect of an increase of density of trapped electrons on the distribution of charges in the active layer and in the bulk electrolyte of a standard DSC. The calculation are performed at short-circuit at 1 sun illumination. The results are obtained adopting the parameterizations in Table II, which was carefully extracted from a detailed comparison of the model with the experimental data.\(^\text{34}\)

Figure 2 shows the calculated charge density profiles inside a DSC at 1 sun illumination intensity for short circuit condition, considering three different situations. The a plot describes a cell where no electrons are trapped, whereas in b and c plots a stepwise increase in the density of traps (\( N_t = 10^{20} \text{ cm}^{-3} \), \( N_t = 10^{21} \text{ cm}^{-3} \)) is considered. The geometric interface between the effective medium and the bulk electrolyte presents some numerical oscillations, due to the abrupt change in porosity. In absence of traps, the electrons show a depletion profile toward the anode contact interface. We want to underline that this concentration gradient is responsible for the electron diffusion current, represented by the first term of Eq. 1. Even though, the ionic charge densities feature a relative flat evolution all along the cell, regardless the type of ionic species. The ionic species are therefore only slightly perturbed by the current generated by the photoelectrons.

The implementation of this calculation with the occurrence of a modest density of traps (\( N_t = 10^{20} \text{ cm}^{-3} \) Fig. 2b, comparable with other works\(^\text{34}\), seems to not significatively alter the distribution of charges inside the cell. Nevertheless, the presence of electrons trapped in a DSC with 10 \( \mu \)m of TiO\(_2\) and 20 \( \mu \)m of bulk electrolyte. Conduction band electrons (black) trapped electrons (dashed black), iodide (red) tri-iodide (green) and the positive cation (blue) are plotted. The profiles are shown in absence of traps (a) and for a trap density \( N_t = 10^{20} \text{ cm}^{-3} \) (b) and \( N_t = 10^{21} \text{ cm}^{-3} \) (c). Calculations are performed at short-circuit condition at 1 sun illumination.

**Table II. List of parameters used to simulate a working DSC.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu_e )</td>
<td>1</td>
<td>([\text{cm}^2/\text{Vs}])</td>
</tr>
<tr>
<td>( k_e )</td>
<td>1000</td>
<td>([\text{s}^{-1}])</td>
</tr>
<tr>
<td>( D_{I^2} )</td>
<td>(10^{-3})</td>
<td>([\text{cm}^2/\text{s}])</td>
</tr>
<tr>
<td>( D_{I^3} )</td>
<td>(10^{-3})</td>
<td>([\text{cm}^2/\text{s}])</td>
</tr>
<tr>
<td>( \bar{n}_{I^2} )</td>
<td>0.45</td>
<td>[Mol/l]</td>
</tr>
<tr>
<td>( \bar{n}_{I^3} )</td>
<td>0.05</td>
<td>[Mol/l]</td>
</tr>
<tr>
<td>( N_t )</td>
<td>(10^{20}, 10^{21})</td>
<td>([\text{cm}^{-3}])</td>
</tr>
<tr>
<td>( a )</td>
<td>0.3</td>
<td>[-]</td>
</tr>
<tr>
<td>porosity</td>
<td>0.5</td>
<td>[-]</td>
</tr>
<tr>
<td>( d_0 )</td>
<td>0.1</td>
<td>([\text{A/cm}^2])</td>
</tr>
</tbody>
</table>

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in the exponential tail forces the positive ion charges to redistribute along the cell. At short circuit the free electron density is bended toward the collector. Since trapped and conduction band electrons are assumed to be in equilibrium, the bending of the two profiles follows the same feature. In this case, the negatively charged electron density (free and trapped) is much larger respect to the case of no traps. This induces the double effect of pushing $I^-$ in the bulk electrolyte and pulling of the positive cation density toward the mesoporous medium. Here the cation follows the electronic depletion as well, in order to assure charge neutrality. Since no cationic current at the anode collector is allowed to flow, (electrochemical potential of $C^+$ is set to be zero at $x = 0$) the density bending of the cation corresponds to a modification of the electrostatic potential. As a consequence, a weak electric field appears at the collector interface ($\sim 1$-10 V/cm). In fact, the high amount of trapped positive cation in the mesoporous region. This spatially distrubution of charges in the electrolyte is more drastically influenced when the density of trapped electrons become higher than the concentration of ions in the electrolyte (Fig. 2c). This high electron density can experimentally take place when there is a lack of percolation among the TiO$_2$ nanoparticles (eg. electrode too porous or bad sintered) or when the cell is exposed to light intensity higher than 1 sun. In this particular case, the cations cannot efficiently screen the excess of negative charges in the TiO$_2$. It results a weak electric field appearing not only within the mesoporous medium, but in the whole cell profile ($\sim 0.1$ V/cm). In fact, the high amount of trapped electrons in TiO$_2$ entails an important depletion in the other negative species ($I^-$ and $I^-$) toward the bulk electrolyte, enforced by an accumulation of positive cation in the mesoporous region. This spatial charge redistribuition in the device has a detrimental effect on its J-V characteristics, as shown with the red curve in Fig. 3. In this case the free electrons density in the conduction band state is severely reduced, and this, as previously remarked, should decrease the recombination. Actually the redistribution of ionic charges due to the electric field, makes the $I^-/I^-$ ratio more relevant in the recombination rate Eq. 7, resulting in an overall augmented and detrimental recombination (inset Fig. 3).

We calculate the current density profiles for each charge carrier and reported the results in Fig. 4. The total current of a DSC device results from the sum of drift current and diffusion current for each charged species. In order to fulfill the charge conservation, the total current must be constant throughout the device.

The fluxes of oxidized and reduced species in the electrolyte are flowing in opposite directions. $I^-_I$ is flowing from the photo-anode to the counter-electrode (giving a negative current) and $I^-_I$ moves from the counter-electrode to the photo-anode, thus providing a positive current by convention. We can extract then the contribution to the total current of the drift and diffusion components. For what concerns electrons, only conduction band electrons participate to transport, therefore the electronic drift current in DSC is negligible. This has been previously demonstrated theoretically and through a comparison with the experimental data. On the other hand, ions in DSC present a far larger density respect to free electrons (Fig. 2), therefore even though the electronic field is weak, it generates a non negligible ionic migration current.

For the $I^-_I$ the drift is representing the 30% of the total $I^-_I$ current, whereas it is the 10% for $I^-_I$ owing to the net charge density difference of the two anions (Fig. 2). The drift component of the current of both species is positive accordingly to the electric field. The behavior

Figure 3. Calculated J-V characteristics in absence of traps (black line), with medium (green) and high (red) concentration of traps. The inset shows the recombination rate profile calculated at open-circuit voltage for the three cases.

Figure 4. Current density profiles for electrons (black) iodide (red) and triiodide (green) are reported in both plots (solid lines). Left plot reports the diffusive (dash) contributions to the total current and the right plot reports the drift (dot) ones. Electronic diffusive current coincides with the total one. The total current of the cell is represented by the pink line.
discussed above is now calculated in a more realistic device in presence of supporting electrolyte. In order to quantify the influence of these additives on the electric field, we increased the concentration of the existent ionic species (already implemented in the code), considering the effect on the Poisson equation only. The initial molarity of $I^-$, $I_3^-$ and $C^-$, noted $[C_0]$, has been increased of 1 and 2 orders of magnitude.

The J-V characteristic profiles (shown in Fig. 5) are unaltered by the presence of such a high density of $I^−$, $I_3^-$ and $C^-$ meaning that all the ionic charges in excess does not contribute to the photo-current and are actually inert for the generation/recombination process. Their role consists mechanistic to screen the macroscopic electric field, which is exactly the role played by an inert supporting salt in electrolyte. This expedient allows us to avoid implementing some more equation in the code to include other inert additives, which is computationally very expensive.

In Fig. 6 the drift ionic currents are finally reported as a function of the inverse of the electric field for $I^−$ and $I_3^-$ with increasing concentration of ionic species. In order to avoid to include additional effects induced by high electric field at the collector, we calculated the mean value of the electric field in the bulk electrolyte side only. As expected, the drift component of the current decreases with a high density of ions in solution. Experimentally the concentration of supporting additives lies in a range of 0.1-1 Mol/L, therefore we can conclude from this work that the ionic drift component of the current cannot be completely suppressed in a working DSC under standard illumination.

Conclusions

In this work we have made use of a drift-diffusion model to provide new insights about the current description of the mass transport in a DSC under operation. We consider out from the model the evolution of the electrostatic field in the cell for different density of trapped electron in TiO$_2$. The main outcome stems from the demonstration of a non-negligible iodide drift current taking place in the mesoporous medium filled by electrolyte. On the other hand, when the supporting electrolyte is included in the simulation, the drift ionic current can be suppressed, but only for very large concentration of additives. This finding shed light not only on the role of additives as supporting electrolyte but also on the importance of charge unbalancing in the photoelectrochemical DSC device.

Acknowledgment

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References


Figure 5. Current voltage characteristics calculated with an enhanced molarity of initial iodide and tri-iodide concentration.

Figure 6. Drift current of $I^-$ (black) and $I_3^-$ (red) are plotted in function of the inverse of mean electric field for three different concentrations of supporting electrolyte.