SIMULATION ANALYSIS OF MULTIPOLAR ENCROACHMENT IN MESOPOROUS PHOTOANODE FOR DYE-SENSITIZED SOLAR CELL

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Abstract:- A simulation model has been presented which describes the transport in dye-sensitized solar cells on a fine scale on the basis of Brownian motion. Simulation tool named Weighted Finite Automata (WFA) has been used for this purpose. The aim of the simulation tool is to determine to what extent a multipolar diffusion transport mechanism can be executed in DSSCs, and to study the basic requirements for such type of coupled transportation. Here mesoporous morphology has been treated as an objective having repetitive network containing mutually connected species.

Keywords – Weighted Finite Automata, multipolar diffusion, Brownian motion

I. INTRODUCTION

TiO_2 has been under immense research because of its potential in various fields [1, 2]. Specifically dye-sensitized solar cells based on TiO_2 have attracted much attention since its breakthrough in 1991 [3]. A typical DSSC consists of TiO_2 layer deposited on to indium tin oxide (ITO) coated glass substrate as working electrode, a photosensitive dye, electrolyte and counter electrode. The performance of DSSC depends significantly on the properties of metal oxide photoanodic film such as crystalline nature, grain size, thickness and porosity. Hence, control of these parameters is conquered by a large number of experimental and theoretical methods [4-6]. Analyses of processes involved in operating mechanism of DSSC are most frequently based on physical models that link material characteristics with the electrical performance of the whole cell [7, 8].

Several models of DSSCs have been traced in the literature with diffusion as dominant charge transport mechanism [9, 10]. From modeling perspectives DSSC is still a challenge because of mesoporous structure that separates the charges but still allows the interactions and charge transfer processes. The presented research article is based on a classical physical model based on simulation tool Weighted Finite Automata (WFA) that takes in to account both diffusion of both electrons and holes in the cell architecture [11].

II. MODELLING AND ANALYSES

Macroscopically, diffusion can be described as mass transport down a concentration gradient. The photocurrent at each point in the photoanode can be given by Fick's law:

$$J(x) = q\,D_{eff}\frac{ds_{CB}(x)}{dx} \tag{1}$$

Here D_{eff} is effective diffusion coefficient.

Since the diffusion coefficient of ions is usually lower than that of electrons in crystalline TiO2, this approach explains why a cation with large diffusion coefficient yields a large effective electron diffusion coefficient; moreover, it also explains the observed ion concentration dependence. Due to the polar nature of the charge neutral electron/ion couple, this transport process is usually referred to as multipolar diffusion. The multipolar diffusion is given by

$$D_{amb} = \frac{n+p}{n/D_p + p/D_n} \tag{2}$$

Here n and p refer correspond to density of electrons and holes respectively. D_n and D_p are their corresponding diffusion coefficients.

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Brownian motion relates spontaneous movements on a fine scale with an effective diffusion coefficient via following equations:

$$(\vec{r} - \vec{r_0})^2 = 6tD_{amb} \qquad (3)$$

$$\overrightarrow{r_{n+1}} - \overrightarrow{r_n} = \Delta\vec{r} \qquad (4)$$

Here, $\vec{r}$ and $\vec{r_0}$ are instantaneous and initial position vector respectively. $\Delta\vec{r}$ is displacement vector and t is total simulated time.

If the medium in which Brownian motion considered is homogeneous, D_{amb}, calculated from Eq. 3, would be equal to D_{bulk}, but by introducing boundary conditions, D_{amb} becomes less than the bulk value. The mesoporous film has been modelled using unit cells, which describes the spatial arrangement of particles. 4-coordinated unit cell can be a besr resemble to mesoporous film as depicted by coordination studies of Benkstein et al. [12]. The porosity was controlled by the necking between neighboring nanoparticles; since the mesoporous film was modelled by unit cells, this could be described by simple analytical expressions. The simulations yielded the quotient D_{amb}/D_{bulk} for electrons and holes as a function of porosity and for the 4-coordinated structure; the results can be picturized in Figure 1.
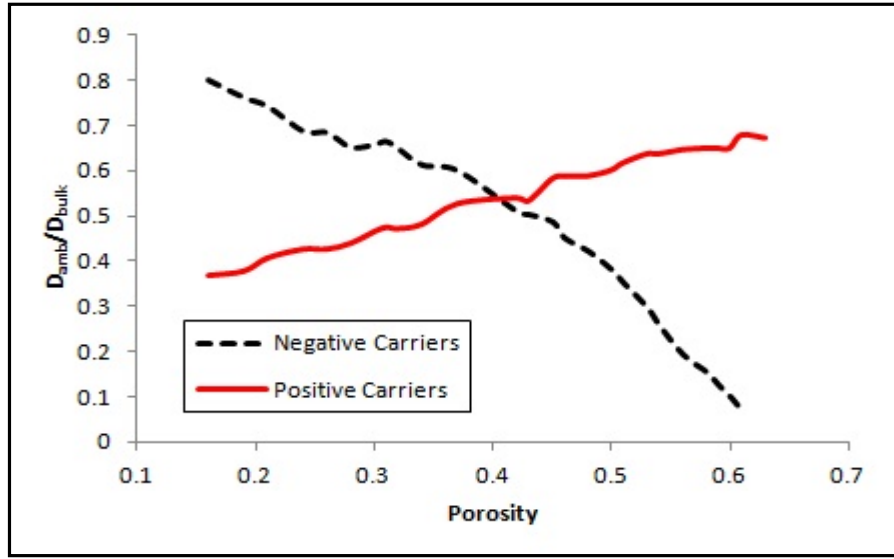

Figure 1. The quotient D_{amb}/D_{bulk} for electrons and holes as a function of porosity

From figure 1 it is clear that D_{amb} is roughly half the bulk value for both type of charges at a porosity value of 0.5. Lowering of ambient diffusion coefficient indicates that these boundary conditions are not adequate to explain the transport in DSSC.

The structure of the mesoporous film was modeled as a 3-dimensional effective medium of infinite area. The cell was divided into regions, in which electron and ionic transport were allowed in the mesoporous region, but only ionic transport was allowed in the electrolyte region. The film thickness, *d*, was further divided into a number of slices. To qualitatively compare the simulation results with presented experimental results, we decided to simulate time of flight (*TOF*) measurements. For such simulations, the time was also divided into timesteps.

The electron and hole currents were described by the combined effects of diffusion and drift. For the electron current, this is expressed in eq. 5.

$$\frac{J(x)}{q} = D_{bulk}\frac{de^-(x)}{dx} + \mu E(x)e^-(x) \qquad (5)$$

Here *E(x)* is electric field and μ is mobility.
To simulate charge generation, the Lambert-Beer law, expressed in eq. 6 was used

$$I = I_0\exp(-x\alpha) \qquad (6)$$

In the simulation it was considered that sunlight was incident from substrate electrode (SE) side and the electrons were generated close to electrode electrolyte (EE) interface. The simulations yielded current versus time

characteristics for low and high concentration of charge carriers at different values of effective permittivity coefficient ε as shown in Figures 2 and 3.
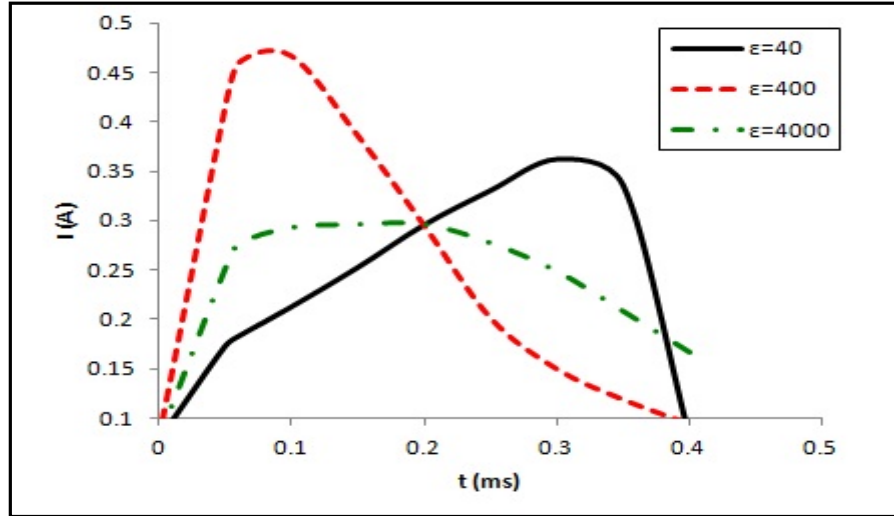

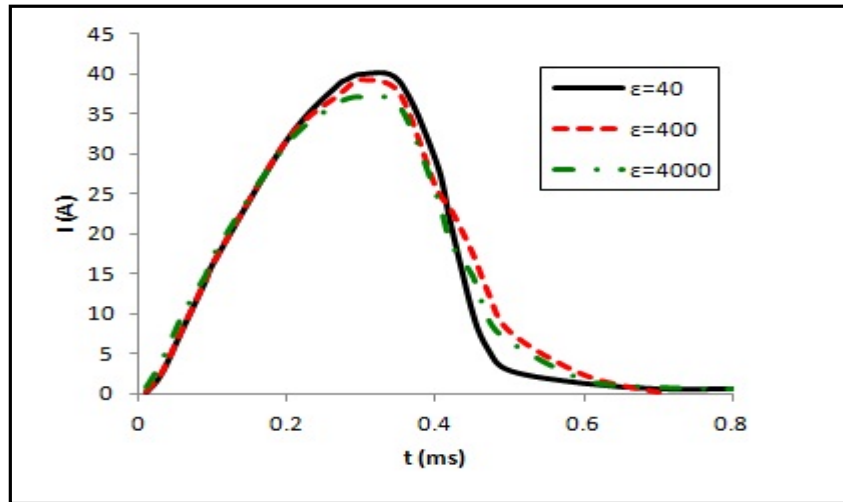Figure 2. Time of Flight response for low concentration of charges

Figure 3. Time of Flight curves for high concentration of charge carriers

For low concentrations of electrons and ions (Figure 2), the deviation from charge neutrality causes small electric fields through the film, transport varies between pure diffusion (no influence of electrostatic interactions) and multipolar diffusion (transport totally controlled by electrostatic interactions). However, when the intensity and ionic strength increases, the transport nature becomes more multipolar, *i.e.*, the bulk diffusion coefficients are too low, compared to the magnitudes of the electric fields, to allow pure diffusion to be a significant component of the overall transport process. Therefore, ε has no influence on the electron transport properties for high light conditions (Figure 3) because the overall transport is determined by electrons-ion couplings.

Moreover, the simulation results explain why the electron diffusion coefficients, when calculated from time of flight (TOF) experiments, are roughly equal in both TiO_2 and ZnO, despite the fact that ε is lower for ZnO [13]. The *WEIGHTED FINITE AUTOMATA (WFA)* model fails, however, to explain the faster transport associated with high light intensities and therefore indirectly supports dominance of trapping/detrapping mechanism as well.

III. CONCLUSIONS

The simulation model has been used for studying the influence of the morphology of the mesoporous film and the influence of electron-ion interactions on electron transport. They cannot, however, be directly applied as

complete DSSC models, because of the difficulty in interpreting the results obtained while using effective parameters. For the purposes of comparison with simulation results and to increase our understanding of the processes operating the DSSCs, various experiments will be carried out.

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