TiO_2 광전극의 흡착 특성이 염료감응형 태양전지 효율에 미치는 영향

황경준[1], 강현철[2], 심왕근[2], 문 희[2], 박경희[3], 김상채[4], 이재욱[1,*]
[1]서남대학교 환경화학공학부, [2]전남대학교 응용화학공학과,
[3]전남대학교 전기공학과, [4]목포대학교 환경교육학과
(jwlee65@naver.com[*])

Influence of TiO_2 adsorption properties on performance of dye-sensitized nanocrystalline solar cells

Kyung-Jun Hwang[1], Hyun-Chul Kang[2], Wang-Geun Shim[2], Hee Moon[2]
Kyung-Hee Park[3], Sang-Chai Kim[4], Jae-Wook Lee[1,*]
[1]Department of Environmental and Chemical Engineering, Seonam University,
[2]Department of Applied Chemical Engineering, Chonnam National University,
[3]Department of Electricity Engineering, Chonnam National University,
[4]Department of Environmental Education, Mokpo National University
(jwlee65@naver.com[*])

INTRODUCTION

Dye sensitized solar cells (DSSCs) have been receiving much attention because they have many advantages such as low cost, less toxic manufacturing, easy scale-up, light weight, and use of flexible panels compared to the conventional p-n junction devices [1,2]. It has been pointed out that further works on the development of nano-structured materials as well as the analysis of the electron transport dynamics should be conducted to enhance the low energy conversion efficiency of DSSC. There have been many studies on the synthesis and characterization of titania nanocrystallites as well as the development of dyes for DSSC. However, systematic studies on the influence of adsorption properties between dye molecules and titania films on the power conversion efficiency of DSSC are very limited.

The aim of this work is to investigate the influence of Ru(II) dye adsorption properties on the conversion efficiency of DSSC. For this purpose, experimental and theoretical studies on the adsorption equilibrium and kinetic studies as functions of solution pH and temperatures were conducted to control the adsorption amount and also understand the adsorption mechanism of N719 dye on nano-structured titania particles. Adsorption kinetic data were analyzed by employing the pseudo-second-order model [3]. In addition, the solar cell performances including the overall conversion efficiency (η), fill factor (FF), open-circuit voltage (V_{oc}) and short-circuit current (I_{sc}) of the TiO_2/dye sensitized nanocrystalline TiO_2 solar cells were investigated in accordance with the adsorption quantity of N719 dye. An equivalent circuit analysis using the one-diode model was used to evaluate the influences of adsorption quantity on the energy conversion efficiency of DSSC [4,5]. A nonlinear least-square optimization method was used to determine five model parameters.

EXPERIMENTAL

Titanium particles of single-phase anatase nanocrystallites were prepared by the hydrolysis

of titanium tetraisopropoxide under acidic condition and characterized by XRD, FE-SEM, AFM and BET analysis. Adsorption equilibrium experiments were carried out by contacting a given amount of TiO_2 with N719 dye solution in a shaking incubator at different temperatures and pH. Solution pH determined by using the pH meter. Zeta potentials of TiO_2 particle in the solution were measured using a zeta potential apparatus. On the one hand, adsorption kinetic experiments of TiO_2 cell were conducted for low and high concentrations of N719 dye in stirring. The adsorption capacity (q) of TiO_2 particles was determined by measuring the dye concentrations before and after adsorption using a UV spectrophotometer after filtration with a membrane filter. On the other hand, the adsorption capacity of TiO_2 film was measured by completely desorbing the adsorbed dye molecules from TiO_2 film using NaOH solution/ethanol. In addition, the current-voltage (I-V) curves were measured using a source measure unit under irradiation of white light from a 100 W lamp. The incident light intensity and the active cell area were 45 $mWcm^{-2}$ and 0.64 cm^2, respectively. The I-V curves were used to calculate the short-circuit current (I_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and overall conversion efficiency (η) of DSSC.

RESULTS AND DISCUSSION

The synthesized TiO_2 films were characterized by TEM, XRD, FE-SEM, and BET analysis[6]. Fig. 1(a) shows a HR-TEM image and electron diffraction pattern of TiO_2 particle. The size of TiO_2 particles is approximately 10~20 nm. The electron diffraction of TiO_2 displays the Debye-Scherrer rings of anatase. The lattice fringes corresponding to the (1 0 1) plane of anatase can be seen in the HR-TEM image. Fig. 1(b) shows the FE-SEM images of cross sectional TiO_2 film. The film thickness is about 8~10 ㎛. According to the AFM image (Fig. 1(c)), the film has heterogeneous surface with a few separated islands.

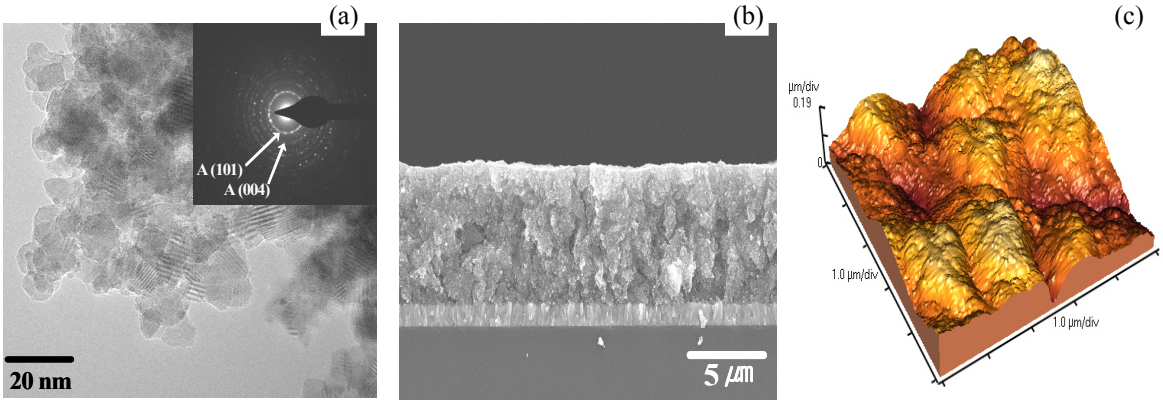

Fig. 1.(a) HR-TEM image and Dffraction pattern of synthesized TiO_2 particle; (b) FE-SEM image and (c) AFM image at synthesized TiO_2 film.

Fig. 2(a) shows the adsorption isotherms for three different temperatures (298.15, 313.15, 333.15 K). The results show that the adsorption capacity increased with increasing temperature. The chemisorption usually requires activation energy which increases with increasing temperature. Finnie et al. [7] have suggested from the vibrational spectroscopic

study of the coordination of Ru(II) dye to the surface of nanocrystalline titania that the chemical bonding structure of dye molecule is a bidentate chelate or bridging coordination to the TiO_2 surface via two carboxylate groups per dye molecule. Fig. 2(b) shows the typical examples of the effect of initial concentrations (0.004, 0.04 mM) on the adsorption kinetics. The adsorption kinetics can be successfully described by the pseudo-second-order model. As the kinetic experimental results, the determined rate constant was 21.089 for low concentration (0.004 mM) and 13.514 g mM^{-1} h^{-1} for high concentration (0.04 mM). Contrary to our expectation, the adsorption kinetics was almost independent of the dye concentrations because of the very fine particles of TiO_2.

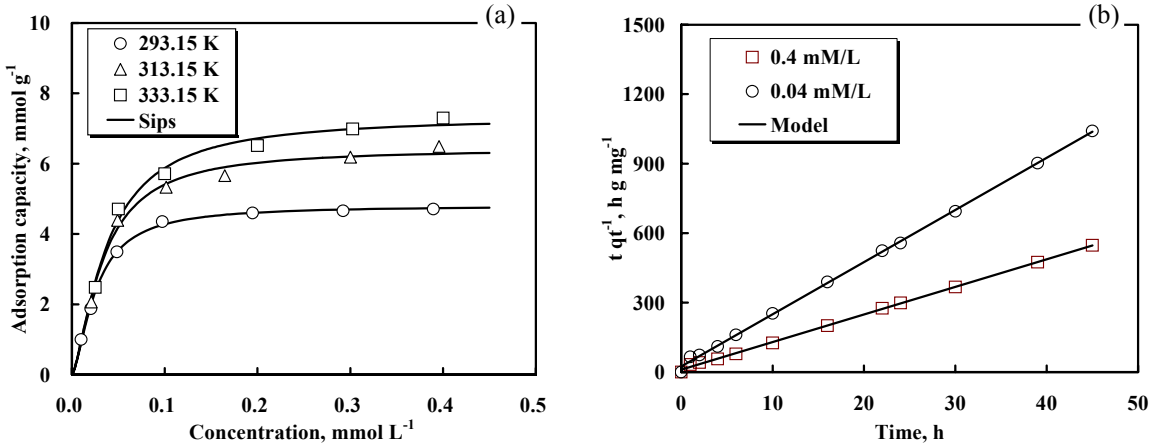

Fig. 2. (a) Adsorption isotherms of N719 on TiO_2 particles in terms of temperatures; (b) Adsorption kinetics of N719 on TiO_2 particles depending on the concentrations.

An accurate knowledge of solar cell parameters from experimental data is of key importance for the design of solar cells and for the estimation of their performance. It has been established that the current-voltage curves of DSSC can be satisfactorily fitted to a 1-diode model for liquid electrolyte and a 2-diode model for polymer electrolyte. The current-voltage relation using a 1-diode model[8] under illumination is given by

$$I = I_{ph} - I_0\left\{\exp\left(\frac{q}{nkT}\left(V + IR_s\right)\right) - 1\right\} - \frac{V + IR_s}{R_{sh}} \qquad (1)$$

where I_{ph} is the photo-generated current, I_o is the diode saturation current (i.e., initial current), n is the diode quality factor (or ideality factor), R_s is the series resistance, R_{sh} is the parallel (shunt) resistance, q is the elementary electric charge (1.602×10^{-19} C), k is the Boltzman constant (1.38×10^{-23} J/K), and T is the temperature. Solar energy conversion efficiency is implicit but cannot be solved analytically. To evaluate five model parameters (I_{ph}, I_o, n, R_s, R_{sh}), we used a nonlinear least-square optimization algorithm based on the Newton's method modified by introducing the so-called Levenberg parameter [9]. The objective function F with respect to the set of unknown parameters u is

$$F(u) = \sum_{i=1}^{n}\left[I_{i,\exp} - I_{i,cal}\left(V_{i,}, u\right)\right]^2 \qquad (2)$$

where u is the unknown parameters $u(I_{ph}, I_o, n, R_s, R_{sh})$, $I_{i,cal}$ and $I_{i,exp}$ are the experimental and calculated current at i-th point, and n is the number of data points. Fig. 3(left) exhibits the flow chart for the calculation step of a nonlinear optimization procedure. The solid lines in Fig. 3(right) are the predicted results using the parameters of 1-diode model. A good agreement between the measured data and the predicted results was observed in the effects of adsorption quantity (Fig. 3(right)) on the photovoltaic performance of DSSC. These findings led us to conclude that the optimal conditions of dye adsorption properties and TiO_2 paste should be carefully determined to increase the conversion efficiency of DSSC.

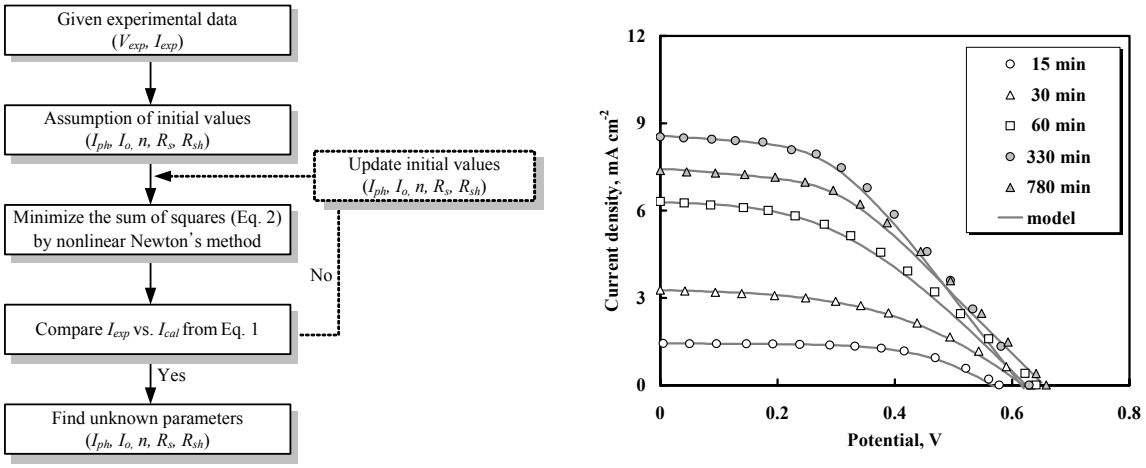

Fig. 3. (left) Flow chart for the calculation of 1-diode model; (right) Photocurrent-voltage (I-V) curves of TiO_2/dye nancocrystalline solar cell depending on adsorption quantity.

REFERENCES

1. T. Hoshikawa, T. Ikebe, M. Yamada, R. Kikuchi, K. Eguchi, *J. Photochem. Photobiol. A* 184, 78 (2006).
2. J. Xia, F. Li, C. Huang, J. Zhai, L. Jiang, *Solar Energy Materials & Solar Cells* 90, 944 (2006).
3. M.H. Kalavathy, T.S. Karthikeyan, L.R. Miranda, *J. Colloid Interface Sci*. 292, 354 (2005).
4. J. A. Anta, F. Casanueva, and G. Oskam, *J. Phys. Chem. B* 110, 5372 (2006).
5. Z. Ouennoughi and M. Murayama, *Solid-State Electronics* 43, 1985 (1999).
6. J. W. Lee, K. J. Hwang, W. G. Shim, K. H. Park, Photocurrent-Voltage of a Dye-Sensitized Nanocrystalline TiO_2 Solar Cells Influenced by N719 Dye Adsorption Properties, *J. Nanoscience and Nanotechnology* (in print, 2007).
7. K.S. Finnie, J.R. Bartlett, J.L. Woolfrey, *Langmuir* 14, 2744 (1998).
8. Z. Ouennoughi and M. Murayama, *Solid-State Electronics* 43, 1985 (1999).
9. J. B. Riggs, *An Introduction to Numerical Methods for Chemical Engineers*, Texas Tech. Uni. Press: Lubbock, 1988.