Influence of electrolytes on the photovoltaic performance of organic dye-sensitized nanocrystalline TiO₂ Solar cells

K. Hara⁺, T. Horiguchi, T. Kinoshita, K. Sayama, H. Arakawa⁺,*

⁺ National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan
* Sumitomo Osaka Cenlent Co. Ltd., 585 Toyotomi, Funabashi. Chiba 274-8601, Japan

Received 4 September 2000; accepted 14 December 2000

Abstract

We have studied the influence of electrolytes on the photovoltaic performance of mercurochrome-sensitized nanocrystalline TiO₂ solar cells using LiI, LiBr, and tetraalkyl-ammonium iodides as the electrolyte. Short-circuit photocurrent density (Jsc) and open-circuit photovoltage (Voc) depended strongly on the electrolyte. Jsc of 3.42 mA cm⁻² and Voc of 0.52 V were obtained for the LiI electrolyte and Jsc of 2.10 mA cm⁻² and Voc of 0.86 V were obtained for the Pr₄NI electrolyte. This difference in photovoltaic performance was due to the change in the conduction band level of the TiO₂ electrode. Large Voc of 0.99 V was obtained for the LiBr electrolyte due to the large energy gap between the conduction band level of TiO₂ and the Br/Br₂ redox potential. Solar cell performance also depended strongly on organic solvent, suggesting that the physical properties of solvents such as Li ion conductivity and donor number affect photovoltaic performance. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Dye sensitization; TiO₂; Solar cell; Mercurochrome; Photoelectrochemical; Electrolyte; Solvent

1. Introduction

Grätzel et al. reported a highly efficient dye-sensitized solar cell based on cisdithiocyanato bis (4,4'-dicarboxy-2,2'-bipyridine) ruthenium (II) (Ru(dcbpy)$_2$(NCS)$_2$),
nanoporous TiO$_2$ thin film electrodes, and an I$^-$/I$_3^-$ redox electrolyte [1-3]. Since then, this dye-sensitization system has been widely studied using different metal complex sensitizers and nanoporous TiO$_2$ electrodes. Because the dye-sensitized nanocrystalline solar cell contains components such as photosensitizers, nanocrystalline semiconductor thin film electrodes, electrolytes, and counter electrodes, we must optimally tune conditions involving these factors to attain maximum cell performance. Electrolytes, such as redox species, counter cations, and solvents, are important factors determining the photovoltaic performance of dye-sensitized solar cells, in addition to the photosensitizer and nanocrystalline semiconductor thin film. Liu et al. investigated the influence of redox species on the interfacial energetics of dye-sensitized nanoporous TiO$_2$ solar cells [4]. They reported the effect of I$_3^-$ concentration and cation species such as Li$^+$, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$ on short-circuit photocurrent density ($J_{sc}$) and open-circuit photovoltage ($V_{oc}$) of the cell. Grätzel et al. reported that imidazolium derivative iodides showed good performance as the electrolyte for the Ru(dcbpy)$_2$(NCS)$_2$-sensitized nanocrystalline TiO$_2$ solar cell [5,6]. A mixture of dimethylhexylimidazolium iodide, LiI, I$_2$, and tert-butylpyridine (TBP) in acetonitrile, for example, has been used for the electrolyte [6]. Their results suggest that properly tuning the electrolyte dramatically improves cell performance.

We have reported good performance of organic dyes such as cosin Y and mercurochrome as the photosensitizer for dye-sensitized nanocrystalline oxide semiconductor solar cells [7-9]. In previous work, we used tetrapropylammonium iodide (TPAI) and I$_2$ in a mixture of acetonitrile and ethylene carbonate as the redox electrolyte. In this work, we have studied the effect of electrolytes such as redox species, counter cations, and solvents on the photovoltaic performance of mercurochrome-sensitized nanocrystalline TiO$_2$ solar cells to improve cell performance and understand better the photovoltaic mechanism.

2. Experimental

2.1. Preparation of TiO$_2$ thin films

A commercial TiO$_2$ nanoparticle (Nippon Aerosil, P25) was used for the electrode material. The TiO$_2$ thin film photoelectrode was screen-printed on a SnO$_2$-coated glass substrate (Nippon Sheet Glass Co., 10Ω/sq, transparency 80%) and then calcined at 500°C for 1 h, as reported previously [9]. A prepared TiO$_2$ thin film was dipped in a 0.1 mol dm$^{-3}$ TiCl$_4$ (Wako Chemicals) aqueous solution for over 18 h at 20°C and then was calcined at 500°C for 1 h in air (TiCl$_4$ treatment). The TiO$_2$ thin film measured using an Alpha-Step 300 profilometer (Tencor Instruments) was 8 μm thick.

2.2. Dye adsorption on oxide semiconductor thin films

A 0.5 mmol dm$^{-3}$ ethanolic solution of mercurochrome was prepared from mercurochrome (Aldrich) and dehydrated ethanol (Wako) without further purification.
The TiO$_2$ thin film was immersed in this solution and then refluxed at 80˚C for 1 h to fix dye on TiO$_2$ electrodes.

2.3. Photoelectrochemical measurements

Reagent-grade chemicals such as LiI (Wako Chemicals), LiBr (Wako), Pr$_4$Nl (Tokyo Kasei), and I$_2$ (Wako) were used for the electrolyte. The organic solvents we used were acetonitrile (AN), propionitrile (PN), methoxyacetonitrile (MAN), methoxypropionitrile (MPN), benzonitrile (BN), phenylacetonitrile (PAN), nitromethane (NM), propylene carbonate (PC), dimethoxyethane (DME), dimethylsulfoxide (DMSO), tetrahydrofuran (THF), N,N-dimethylformamide (DMF), N-methyl-2-pyrididone (NMP), methylalcohol (MeOH), ethylalcohol (EtOH), methoxyethylalcohol (MEtOH), 1-propylalcohol (1-PrOH), iso-propylalcohol (2-PrOH), 1-butylalcohol (1-BuOH), 1-hexylalcohol (1-HeOH), and ethylene glycol (EG). Chemicals and solvents were used without further purification.

The 2-electrode sandwich cell for photovoltaic measurement consisted of a dye-adsorbed TiO$_2$ electrode, a counter electrode, a spacer, and an organic electrolyte. The counter electrode was a Pt film sputtered on SnO$_2$-coated glass using an ion coating machine (Eiko Engineering, IB-5). The spacer was polyethylene thin film 120 µm thick. The apparent surface area of mercurochrome-adsorbed TiO$_2$ electrodes was 1.0 cm$^2$ (1.0 x 1.0 cm). The photoelectrochemical performance of solar cells was measured with a potentiostat/galvanostat (Nikko Keisoku, NPGS-2501), a digital multimeter (Escort, EDM-2116), and a XY recorder (Graphtec, WXI 100). The light source was a 500 W Xe lamp with a < 420 nm cutoff filter and a ND 25 filter. The incident light intensity estimated using a thermopile (Eppley Lab., Inc., Newport, RI), was 84 mW cm$^{-2}$.

3. Results and discussion

3.1. Effect of electrolytes

Fig. 1 shows the effect of electrolytes on $J_{sc}$ and $V_{oc}$ for a mercurochrome-sensitized nanocrystalline TiO$_2$ Solar cell under 84 mW cm$^{-2}$ irradiation. The concentration of the electrolyte was 0.3 moldm$^{-3}$ in AN. $J_{sc}$ Of 3.42 mAcm$^{-2}$ and $V_{oc}$ of 0.52 V were obtained in the LiI solution. Smaller $J_{sc}$ and larger $V_{oc}$ compared to those in the LiI solution were observed in tetraalkylammonium iodide (TAAI) solutions: $J_{sc}$ was 2.10 mAcm$^{-2}$ and $V_{oc}$ was 0.86 V in the tetrapropylammonium iodide (TPAI) solution, for example. Quite small $J_{sc}$ in the tetramethylammonium iodide (TMAI) solution was due to the low solubility of TMAI in AN.

To determine the conduction band level of the TiO$_2$ electrode in LiI and TAAI solutions, we conducted cyclic voltammetry for a nanocrystalline TiO$_2$ thin film electrode under UV light irradiation in different solutions. The onset of anodic photocurrent in the LiI solution was about −0.5 V vs. Ag/AgCl (−0.3 V vs. NHE), while that in the TPAI solution was −0.9 V vs. Ag/AgCl (−0.7 V vs. NHE). This
Fig. 1. Dependence of $J_{sc}$ and $V_{oc}$ of a mercurochrome-sensitized nanocrystalline TiO$_2$ solar cell on electrolytes.

indicates that the conduction band level of the nanocrystalline TiO$_2$ electrode in the LiI solution is 0.4V more positive than that in the TPAI solution because the onset of the anodic photocurrent is close to the conduction band level. Zaban et al. measured the potential-dependent photoluminescence of Ru(II)(4,4'-dicarboxylic acid-2,2'-bipyridine)$_2$(4,4'-dimethyl-2,2'-bipyridine) complex adsorbed on a nanoporous TiO$_2$ electrode in an electrolyte solution of LiClO$_4$ and tetrabutylammonium perchlorate (TBAP) [10]. Emission intensity increased with negative potential scanning, indicating that electron injection from the dye into the conduction band of TiO$_2$ is suppressed by applied negative bias. In the TBA$^+$ solution, the onset potential of emission increase is about 0.4V more negative than the onset potential in the Li$^+$ solution, indicating that the conduction band level of TiO$_2$ in the Li$^+$ solution is 0.4V more positive than that in the TBA$^+$ solution. Their result agrees well with our result. The positive shift of the conduction band of TiO$_2$ in the Li$^+$ solution is considered due to intercalation of Li cations into the TiO$_2$ electrode [2, 11-14].

Liu et al. reported the effect of cation species such as Li$^+$, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$ on $J_{sc}$ and $V_{oc}$ of a dye-sensitized TiO$_2$ Solar cell [4]. Largest $J_{sc}$ and smallest Voc were obtained in the Li$^+$ solution compared to those in other cation species, and Voc is proportional to the ionic cation radius. The adsorption of cation species onto the TiO$_2$ Surface leads to the potential drop in the Helmholtz layer, which depends on adsorbed cations and increases with decreasing cation radius. This potential drop causes a positive shift in the conduction band level of the TiO$_2$ electrode depending on the cation species [4, 11, 12].
Fig. 2 shows the energy diagram of a mercurochrome-sensitized TiO₂ Solar cell in LiI and TPAI solutions. The HOMO level of mercurochrome estimated electrochemically was about 0.84V and the LUMO level was -1.20V vs. NHE [9]. The conduction band level of the TiO₂ electrode shifts positively in the LiI solution, increasing the energy gap between the LUMO level of mercurochrome and the conduction band of TiO₂. A larger photocurrent in the LiI solution compared to that in the TPAI solution (Fig. 1), is due to an increase in the driving force for the electron injection process from the LUMO of mercurochrome into the conduction band of TiO₂. 

A larger photocurrent in the LiI solution compared to that in the TPAI solution (Fig. 1), is due to an increase in the driving force for the electron injection process from the LUMO of mercurochrome into the conduction band of TiO₂. 

For a LiBr electrolyte, \( J_{sc} \) of 1.33mAcm⁻² and \( V_{oc} \) of 0.82V were obtained (Fig. 1). The redox potential of Br⁻/Br₂ is 0.85V vs. SCE (0.65V vs. NHE) [15], which is 0.25V more positive than that of I⁻/I₃⁻ redox, resulting in larger \( V_{oc} \) compared to that in iodine redox electrolytes. Small \( J_{sc} \) compared to that in the iodine redox electrolyte suggests that electron transfer from Br⁻ ions into the HOMO of mercurochrome is ineffective because of the small energy gap between the bromine redox potential and the HOMO level of mercurochrome.

Fig. 2. Energy diagram of a mercurochrome-sensitized nanocrystalline TiO₂ Solar cell in LiI and TPAI solutions.
3.2. Concentration effect of LiI and I$_2$

Fig. 3 shows the dependence of $J_{sc}$ and $V_{oc}$ for a mercurochrome-sensitized TiO$_2$ solar cell on LiI concentration in the electrolyte with 0.03 mol dm$^{-3}$ I$_2$ and AN solvent. An increase in LiI concentration from 0.007 to 0.3 mol dm$^{-3}$ leads to an increase in $J_{sc}$ from 0.12 to 4.42 mA cm$^{-2}$ (Fig. 3). This is considered due to the increase in conductivity of the electrolyte with increasing Li$^+$ and I$^-$ concentration. This also suggests that I$^-$ diffusion from the bulk solution into the inside of the nanoporous TiO$_2$ electrode and/or of I$_3^-$ produced by oxidation of I$^-$, from within the nanoporous TiO$_2$ electrode into the Pt counter electrode, are the rate determining steps under these conditions. Under LiI concentration exceeding 0.3 mol dm$^{-3}$, $J_{sc}$ decreased with increasing concentration. This is due to the increase in viscosity of the solution, which decreases ion mobility in the solution, resulting in a small photocurrent. $V_{oc}$ increased with increasing LiI concentration from 0.005 to 0.05 mol dm$^{-3}$ (0.62 V for 0.05 mol dm$^{-3}$) and then decreased to 0.40 V for 3 mol dm$^{-3}$. According to the following equation I$_3^-$ concentration increases with increasing I$^-$ concentration.

$$\text{I}^- + \text{I}_2 \rightarrow \text{I}_3^-.$$  

(1)

$V_{oc}$ for dye-sensitized solar cells with an iodine redox electrolyte is represented by the following equation [1,2]:

$$V_{oc} = \frac{kT}{e} \ln \left( \frac{I_{inj}}{n_{cb}k_c[I^-]} \right),$$  

(2)

![Graph showing the dependence of $J_{sc}$ and $V_{oc}$ on LiI concentration](image)

**Fig. 3.** Dependence of $J_{sc}$ and $V_{oc}$ of a mercurochrome-sensitized nanocrystalline TiO$_2$ Solar cell on the LiI concentration in a 0.015 mol dm$^{-3}$ I$_2$ acetonitrile solution.
where \( I_{\text{inj}} \) is the injection current from dye to semiconductor, \( n_{\text{cb}} \) is the carrier (electron) density on the conduction band of semiconductor, and \( k_{\text{ct}} \) represents the rate constant of reduction of \( I_3^- \) to \( I^- \) (back electron transfer reaction, represented by Eq. (3)).

\[
I_3^- + 2e_{\text{cb}} \rightleftharpoons 3I^- .
\]  

(3)

According to Eq. (2), \( V_{\text{oc}} \) decreases with an increasing back electron transfer reaction. Decrease in \( V_{\text{oc}} \) with increasing LiI concentration is explained by the enhanced back electron transfer reaction.

Dependence of \( J_{\text{sc}} \) and \( V_{\text{oc}} \) of a mercurochrome-sensitized TiO\(_2\) Solar cell on I\(_2\) concentration in a 0.3 mol dm\(^{-3}\) LiI of the AN solution is shown in Fig. 4. \( J_{\text{sc}} \) reached 4.66 mA cm\(^{-2}\) in the 0.015 mol dm\(^{-3}\) I\(_2\) electrolyte and then decreased remarkably with increasing I\(_2\) concentration due to increased viscosity of the solution. In addition, I\(_2\) also absorbs visible light from 400 to 500 nm, suppressing visible light absorption by mercurochrome. \( V_{\text{oc}} \) decreased with increasing I\(_2\) concentration from 0.50 V at 0.005 mol dm\(^{-3}\) to 0.20 V at 1 mol dm\(^{-3}\). An increase in I\(_3^-\) concentration as represented by Eq. (1) enhanced the back electron transfer reaction, decreasing \( V_{\text{oc}} \).

### 3.3. Effect of solvent

Table 1 represents the photovoltaic performance of a mercurochrome-sensitized TiO\(_2\) Solar cell with an iodine redox electrolyte (0.3 mol dm\(^{-3}\) LiI-0.015 mol dm\(^{-3}\) I\(_2\))

![Dependence of \( J_{\text{sc}} \) and \( V_{\text{oc}} \) of a mercurochrome-sensitized nanocrystalline TiO\(_2\) Solar cell on the I\(_2\) concentration in a 0.3 mol dm\(^{-3}\) LiI acetonitrile solution.](image-url)

**Fig. 4.** Dependence of \( J_{\text{sc}} \) and \( V_{\text{oc}} \) of a mercurochrome-sensitized nanocrystalline TiO\(_2\) Solar cell on the I\(_2\) concentration in a 0.3 mol dm\(^{-3}\) LiI acetonitrile solution.
in different organic solvents. Larger photocurrent densities were obtained in nitrile solvents: 3.42 mA cm\(^{-2}\) for AN and 3.23 mA cm\(^{-2}\) for MAN. \(V_{oc}\) for nitrile solvents were about 0.5 V, lesser than that for other solvents. Larger \(V_{oc}\) exceeding 0.8 V was obtained for DMSO (0.85 V), DMF (0.82 V), and NMP (0.80 V) while \(J_{sc}\) was lesser than that for nitrile solvents. It has been shown that \(V_{oc}\) of Ru(dcbpy)\(_2\)(NCS)\(_2\)-sensitized TiO\(_2\) Solar cells increased with treatment of the TiO\(_2\) Surface with pyridine derivatives such as TBP or the presence of TBP in the electrolyte [1,2,16]. Increase in \(V_{oc}\) is attributed to the negative shift in the conduction band of the TiO\(_2\) electrode due to adsorption of basic TBP, in addition to suppression of the dark current (i.e., \(I_{3^-}\) reduction with injected electron represented by Eq. (3)). The conduction band level of the TiO\(_2\) electrode would also be shifted negatively in basic solvents such as DMSO, DMF, and NMP. Mercurochrome was partially desorbed from the TiO\(_2\) surface into DMSO, DMF, and NMP after photovoltaic measurement, while no desorption was observed for nitrile solvents. This is also due to the basic property of these solvents. In alcoholic solvents such as MeOH and EtOH, lesser \(J_{sc}\) below 2 mA cm\(^{-2}\) was obtained and \(V_{oc}\) exceeded 0.7V. \(J_{sc}\) and \(V_{oc}\) in alcoholic

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dye solubility</th>
<th>(J_{sc}) (mA cm(^{-2}))</th>
<th>(V_{oc}) (V)</th>
<th>Fill factor</th>
<th>(\eta) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_2)CN (AN)</td>
<td>Insoluble</td>
<td>3.42</td>
<td>0.52</td>
<td>0.58</td>
<td>1.23</td>
</tr>
<tr>
<td>C(_2)H(_4)CN (PN)</td>
<td>Insoluble</td>
<td>2.62</td>
<td>0.58</td>
<td>0.52</td>
<td>0.94</td>
</tr>
<tr>
<td>CH(_2)O-CH(_2)CN (MAN)</td>
<td>Insoluble</td>
<td>3.23</td>
<td>0.51</td>
<td>0.55</td>
<td>1.08</td>
</tr>
<tr>
<td>CH(_3)O-C(_2)H(_5)CN (MPN)</td>
<td>Insoluble</td>
<td>3.17</td>
<td>0.54</td>
<td>0.44</td>
<td>0.90</td>
</tr>
<tr>
<td>C(_6)H(_5)CN (BN)</td>
<td>Insoluble</td>
<td>1.76</td>
<td>0.51</td>
<td>0.17</td>
<td>0.18</td>
</tr>
<tr>
<td>C(_6)H(_5)-C(_2)H(_5)CN (PAN)</td>
<td>Insoluble</td>
<td>2.20</td>
<td>0.55</td>
<td>0.28</td>
<td>0.40</td>
</tr>
<tr>
<td>CH(_3)NO(_2) (NM)</td>
<td>Insoluble</td>
<td>2.22</td>
<td>0.45</td>
<td>0.58</td>
<td>0.69</td>
</tr>
<tr>
<td>Propylene carbonate (PC)</td>
<td>Insoluble</td>
<td>2.62</td>
<td>0.58</td>
<td>0.49</td>
<td>0.89</td>
</tr>
<tr>
<td>Dimethoxyethane (DME)</td>
<td>Insoluble</td>
<td>2.85</td>
<td>0.55</td>
<td>0.42</td>
<td>0.78</td>
</tr>
<tr>
<td>Dimethylsulfoxide (DMSO)</td>
<td>Soluble</td>
<td>1.40</td>
<td>0.85</td>
<td>0.66</td>
<td>0.94</td>
</tr>
<tr>
<td>Tetrahydrofuran (THF)</td>
<td>Soluble</td>
<td>2.94</td>
<td>0.60</td>
<td>0.32</td>
<td>0.67</td>
</tr>
<tr>
<td>N,N-Dimethylformamide (DMF)</td>
<td>Soluble</td>
<td>2.30</td>
<td>0.82</td>
<td>0.59</td>
<td>1.32</td>
</tr>
<tr>
<td>N-Methyl-2-pyridolone (NMP)</td>
<td>Soluble</td>
<td>2.54</td>
<td>0.80</td>
<td>0.36</td>
<td>0.87</td>
</tr>
<tr>
<td>CH(_3)OH (MeOH)</td>
<td>Soluble</td>
<td>1.30</td>
<td>0.82</td>
<td>0.68</td>
<td>0.86</td>
</tr>
<tr>
<td>C(_2)H(_5)OH (EtOH)</td>
<td>Soluble</td>
<td>2.16</td>
<td>0.77</td>
<td>0.69</td>
<td>1.37</td>
</tr>
<tr>
<td>CH(_3)O-C(_2)H(_5)OH (MEtOH)</td>
<td>Soluble</td>
<td>3.10</td>
<td>0.74</td>
<td>0.58</td>
<td>1.58</td>
</tr>
<tr>
<td>C(_3)H(_7)OH (1-ProH)</td>
<td>Soluble</td>
<td>2.06</td>
<td>0.75</td>
<td>0.60</td>
<td>1.10</td>
</tr>
<tr>
<td>(CH(_3))(_2)CHOH (2-ProOH)</td>
<td>Soluble</td>
<td>1.76</td>
<td>0.70</td>
<td>0.45</td>
<td>0.66</td>
</tr>
<tr>
<td>C(_4)H(_9)OH (1-KetOH)</td>
<td>Soluble</td>
<td>1.94</td>
<td>0.72</td>
<td>0.48</td>
<td>0.80</td>
</tr>
<tr>
<td>C(_5)H(_11)OH (1-HeOH)</td>
<td>Soluble</td>
<td>0.78</td>
<td>0.70</td>
<td>0.42</td>
<td>0.27</td>
</tr>
<tr>
<td>(CH(_2)OH)(_2) (EG)</td>
<td>Soluble</td>
<td>0.92</td>
<td>0.77</td>
<td>0.72</td>
<td>0.61</td>
</tr>
</tbody>
</table>

Electrolyte: 0.3 mol dm\(^{-3}\) LiI-0.015 mol dm\(^{-3}\) I\(_2\). Photoelectrode: TiO\(_2\)/F-SnO\(_2\) (1.0 \(\times\) 1.0 cm\(^2\)). Light source: Xe lamp with \(<420\) nm cutoff and ND25 filters (84 mW cm\(^{-2}\)).
solvents were unstable and decreased dramatically with increasing irradiation time. Dye desorption was also observed in alcoholic solvents after photovoltaic measurement.

Fig. 5 shows $J_{sc}$ of a mercurochrome-sensitized TiO$_2$ Solar cell as a function of the Li$^+$ mol conductivity of solvents [17]. $J_{sc}$ increases with increasing Li$^+$ mol conductivity of solvents. Larger $J_{sc}$ was obtained for AN and NM having large Li$^+$ mol conductivity. The relationship between $V_{oc}$ and the donor number of solvents [18,19] is shown in Fig. 6. Large donor number (i.e., high basic property) leads to a negative shift in the conduction band level of the TiO$_2$ electrode, producing large $V_{oc}$. These results indicate that physical properties of solvents of electrolyte markedly affect the photovoltaic performance of dye-sensitized solar cells.

Table 2 shows the dependence of the cell performance with a bromine redox (0.3 mol dm$^{-3}$ LiBr-0.004 mol dm$^{-3}$ Br$_2$) on the solvent of the electrolyte. Quite small $J_{sc}$ was obtained in a bromine redox electrolyte. Maximum $J_{sc}$ is 1.33mAcm for AN, lesser than that in the iodine redox electrolyte. $V_{oc}$ exceeding 0.8V was obtained, however, in all solvents and maximum $V_{oc}$ reached 0.99 V in DMF. Larger $V_{oc}$ is derived from the more positive redox potential of Br$^-$/Br$_2$ than the iodine redox, resulting in a larger energy gap between the conduction band of TiO$_2$ and the redox potential, as described above. Lesser $J_{sc}$ in bromine redox electrolytes leads to low solar energy conversion efficiency, while larger $V_{oc}$ was obtained. Desorption of mercurochrome from the TiO$_2$ Surface was observed in the Br$^-$/Br$_2$ redox regardless of the solvent.

![Image](image_url)

**Fig. 5.** $J_{sc}$ of a mercurochrome-sensitized nanocrystalline TiO$_2$ Solar cell as a function of the limiting conductance of Li$^+$ of different organic solvents.
As mentioned above, electrolyte parameters such as the redox species, counter cations, and solvents markedly affect the photovoltaic performance of mercurochrome-sensitized nanoporous TiO₂ Solar cells. Changes in photovoltaic properties are mainly explained by changes in the conduction band level of the TiO₂ electrode and differences in the physical properties of solvents such as ion conductivity and donor number. In this work, good solar energy-to-electricity conversion efficiency, \( \eta \), was mainly obtained when \( J_{sc} \) is relatively low and \( V_{oc} \) is relatively large because a
good fill factor is obtained in this condition. For large \( J_{sc} \) and low \( V_{oc} \), \( \eta \) was relatively low due to the low fill factor. To improve \( \eta \), three parameters, \( J_{sc} \), \( V_{oc} \), and the fill factor, must be increased simultaneously. To do this, tuning of the electrolyte is very important in addition to a study of photosensitizers and semiconductor photoelectrodes.

4. Conclusions

Solar cell performance of mercurochrome-sensitized nanoporous TiO\(_2\) Solar cells depended greatly on the electrolyte. \( J_{sc} \) of 3.42mAcm\(^{-2}\) and \( V_{oc} \) of 0.52V were obtained for the LiI electrolyte while \( J_{sc} \) was 2.10mAcm\(^{-2}\) and \( V_{oc} \) was 0.86V for tetrapropylammonium iodide. This difference in photovoltaic performance was explained by the change in the conduction band level of the TiO\(_2\) thin film electrode. Large \( V_{oc} \) of 0.99 V was obtained for the LiBr electrolyte due to the large energy gap between the conduction band level of TiO\(_2\) and the Br\(^{-}\)/Br\(_2\) redox potential. Cell performance also depended strongly on the solvent, suggesting that the physical properties of solvents such as Li ion mol conductivity and donor number affect the photovoltaic property.

References