Highlight Review

Light Energy Conversion and Storage with Soft Carbonaceous Materials that Solidify Mesoscopic Electrochemical Interfaces

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(Received January 12, 2007; CL-078001)

Abstract

Photoactive interfaces created by mesoscopic materials realize high-efficiency light to electric conversion as achieved by dye-sensitized photoelectrodes. Combinaiton of soft carbon composite materials with the mesoscopic interfaces enables solidification of the electrochemical charge-transfer interfaces and incorporation of energy storage function. New approaches for solid-state photoelectrochemistry are described.

♦ Introduction: Carbons as Soft Porous Conductors

Carbonaceous materials have been extensively used in electrochemical industries for their high electro-conductivity, catalytic activity, chemical stability, and low-cost availability in mass production. Softness of carbonaceous conductive powders is prerequisite to preparing a thin redox-active layer on a battery electrode sheet by mechanical compression of the layer holding active materials in a matrix of carbons and polymer binders. In commercial rechargeable cells, carbonaceous materials serve as high-capacity storage materials; typically, lithium-ion batteries use graphite as lithium reservoirs at the negative electrode[1] and capacitors employ activated carbon as electric-double-layer charge storage material.[2,3] Both types of electrochemical cells utilize the conductivity and soft porous nature of these particulated carbons simultaneously. Pore size distributions of the carbon particles vary from the microporous range of less than 2 nm to macroporous range of more than 50 nm. Activated carbon has microporous surfaces yielding extremely high specific area of 1000–2500 $m^2\,g^{-1}$. Acetylene black, a typical carbon black, possesses much lower surface area (20–300 $m^2\,g^{-1}$) but exhibits high electro-conductivity (10^{-1} ohm cm). The latter is available as a powder comprising aggregates of nano-particles with the size range 3–500 nm. Coating of fine carbon particles dispersed in suitable liquid media forms a soft flexible film, which can make good physical contact under mechanical compression with non-smooth or porous surfaces of hard inorganic materials.

Preparation of carbon-based composite materials by hybridizing nano-carbons with organic compounds has contributed to creation of new conductive materials and electronic devices. Nano-carbon materials, nano-graphite and nanotubes, have been extensively studied for applications to electrochemical devices.[4–6] Dispersion of nanotubes in fluid media of ionic liquid has been found to form highly viscous quasi-solid materials which function as excellent ionic conductors.[5,6]

Based on the treatise of photoelectrochemistry, we have recently attempted various studies in light energy conversion and storage by using carbonaceous materials as main elements of layered structures, in which electron/hole separation proceeds across junctions of conductive carbons and metal oxide semiconductors. This review will introduce two typical systems, which utilize solid–solid junctions involving soft porous carbons at the electrochemical interface. One is concerned with solidification of the dye-sensitized solar cell, now extensively studies using mesoporous TiO_2 films. The other is the design of photo-rechargeable cells, photocapacitor, which was invented by us as a unique photovoltaic cell capable of simultaneous electric generation and storage.

♦ Carbon-based Solid-state Photoelectrochemical Cells

Dye-sensitized solar cell (DSC), the photoelectrochemical cell using dye monolayer-coated mesoscopic semiconductor electrodes, is a sole kind of solar cell fabricated under the ambient atmosphere without needs of vacuum preparation processes. Well-made DSCs on glass substrates achieve power conversion efficiency under intense sunlight up to 11%,[7,8] which is significantly high and twice more than the top efficiency of organic photovoltaic cells.[9] Particular advantage of DSC is the low-cost rapid manufacturing system. Coating and patterning of photovoltaic layers can be made by screen printing machines without multiple coating processes. Consumption of the semiconductor material, TiO_2, is only 10–20 $g\,m^{-2}$ for 50-W power output (5% efficiency) without a loss of causing useless parts, which is extremely small compared to the case of crystalline silicons. Without particular improvement to material preparation, 5 to 8% efficiency is obtained without difficulty using Ru bipyridyl complex dyes as sensitizers.[10] Utility-type modules of DSC with series DC connection have demonstrated high performance in utilizing diffused (scattered) sunlight,[11–13] owing to low reflectance index of the surface of porous dye–TiO_2 layers.

Difficulty of the DSC technology, however, exists in ensuring ample durability of the cell. Assessment of durability often cites amorphous silicon (a-Si) photovoltaic cell as a reference, both cells having similar spectral sensitivity to sunlight in the visible wavelength region of <800 nm. While the commercial a-Si cells are durable for years, lifetimes of DSCs are reportedly around 1000 h[14]–1200 h[15] (accelerated test at 80–85 °C).[16] Prac-

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tical lifetimes of DSCs are seriously affected by the gas barrier ability of sealer and kinds of electrolyte composition. Not only are the material of sealer, also the interface of sealer and electrode substrate often involved in the leakage of gaseous components (solvents of electrolytes).

To overcome this problem, solidification of DSC has been attempted by replacing the liquid elements of electrolyte with quasi-solid or solid conductive materials. A smart practice was shown by Tennakone et al.[17] using p-type inorganic semiconductors that act as hole collectors for direct reaction with oxidized dye molecules. Use of CuI[17] and CuSCN[18] achieved 4.5 and 2.0% power conversion efficiencies, respectively. However, filling of the mesoporous interior of TiO_2 with solid inorganic particles is hardly completed when the TiO_2 layer becomes thick ($>3\,\mu m$).[18] To cope this, mixtures of CuI with ionic liquids[19] and organic salts[20] that help to fill the mesopore have also been attempted. Besides the pore filling difficulty, CuI and CuSCN are not chemically very stable against oxidation and dissolution. As alternatives to solid conductors, ionic liquids have been employed as non-volatile liquid media to quasi-solidify the electrolyte layer. Viscous electrolytes can be obtained by mixing ionic liquids with gelling agents[21] and polymer materials,[22] which are capable of yielding 5.0–5.3% efficiency. Quasi-solid-state DSCs fabricated with the ionic liquid-based polymer electrolyte and the Ru complex dye, Z907, show good thermostability and durability on accelerated aging at 80 °C for 1000 h.[14] This result shows that solidification of the cell excluding volatile electrolytes actually improves the lifetime.

The above practices commonly employ the triiodide/iodine couple as an indispensable redox shuttle that electrically combines the dyed TiO_2 surface and solid hole conductors. Further, a counter-electrode material of ample catalytic activity becomes indispensable for ejecting electron to iodine: platinum for this purpose is generally used, which simultaneously acts as catalyst and electron conductor. Unfortunately, however, the use of iodine can be an origin for low stability and short lifetime of the cell, especially at elevated temperatures. Iodine oxidizes most of high-conductive metals (Cu, Ag, Fe, Zn, Ni, Al, Au, etc.). Pt that has sufficient stability even slowly undergoes dissolution through reaction with the electrolyte. Damage of iodine also extends to dissolution of indium–tin–oxide (ITO), the metal oxide conductive layer widely employed on plastic electrode substrates. Further, iodine can be sublimed leading to leakage of electrolyte.

A breakthrough to the above two subjects, efficiency improvement by pore filling and elimination of iodine damage, is to solidify the cell by using a soft organic hole conductor that can penetrate into the depth of mesopores through molecular diffusion and by eliminating the triiodide/iodine redox system. This approach is also promising for realizing a flexible solar cell, which is a recent trend in the advanced DSC researches.[23–26] Development of iodine-free soft hole conductors enables fabrication of solid-state plastic DSC, which is a goal of our recent work for low-temperature preparation of mesoporous TiO_2 on ITO-coated plastic electrodes.[27–30] A challenge of using a solid-state iodine-free organic layer has been reported by Grätzel's group, who used as an organic hole conductor a doped spirobifluorene derivative bearing bulky groups, the latter suppressing the crystallization of molecule that disturbs the pore filling process. This iodine-free quasi-solid-state cell yielded conversion efficiency of 0.74%.[31] The best efficiency of 3.2% has later been reached by improvement of this system, where a thin 2-μm mesoporous TiO_2 film was soaked with a spin-coated mixture of hole conductor and liquid *tert*-butyl pyridine (TBP).[32] The above trials and basically poor penetration of polymers into mespopores[33] teach that the filling of mosoporous interiors need assistance of a fluid component that can help hole transfer from the dye molecule to the surface of a solid conductor.

Our first solution to fabricating a solid-state DSC was combining a hole-transporting polymer, poly(*N*-vinylcarbazole) (PVK), with potassium iodide as a solid-state redox compound that fills the interior of mesopore.[34] On a conductive FTO (F-doped SnO_2) glass electrode (sheet resistance, $10\,\Omega$ per square), we coated a $7\,\mu m$-thick mesoporous TiO_2 layer by sintering a nanocrystalline TiO_2 paste (Solaronix, SA) at 550 °C for 30 min. After sensitization by monolayer adsorption of a ruthenium complex dye (N719), *cis*-bis(thiocyanato-*N*)bis(4,4′-tetrabutylammonium hydrogen dicarboxylato-2,2′-bipyridine-K^2N)ruthenium(II) the dyed mesoporous layer was subjected to pore filling. KI was added into the mesopore as a dilute organic solution in acetonitrile. After repeated addition and drying, the KI-filled TiO_2 mesopore was coated with PVK (0.01–0.1-μm thick) by casting a dichloromethane solution (1.0 mg/mL). Now, we virtually prepared junction of dyed mesoporous TiO_2 and polymer hole conductor. The final step is to ensure an electrical contact with a counter-electrode at the top of the soft polymer layer. Conventional manner has been vacuum deposition of a metal layer such as Au.[31,32] However, we adopted a soft carbon layer as an alternative. An amply thick (300 μm) carbon layer was deposited on the PVK layer, which comprises graphite powder and polyvinylidene fluodide (19:1 in weight). It was coated in the form of a paste dispersing the solid components in dimethylformamide followed by evaporation and annealing at 80 °C. A metallic current collector (vacuum-deposited Pt layer on conductive F/SnO_2 glass) was finally attached to the carbon surface. The soft graphite layer can ensure tight contact with the soft PVK layer and the hard metallic counter-electrode. With this heterojunction cell, we could obtain relatively high performance, yielding a power efficiency of 2.4% in irradiance of $23\,mW/cm^2$ (1/4 sun) (AM 1.5).[34]

Carbonaceous materials not only give an ease in creating good physical contact with soft organic materials but also function as efficient carrier collectors at the porous interface. Difficulty in applying a polymer hole conductor for solidification is that hole diffusion length in most polymer materials is limited to less than 100 nm. This requires a thinnest possible film of a polymer to be involved in the heterojunction structure. With the dye-sensitized porous TiO_2, however, it is geometrically impossible to cover the uneven porous surface with an ultra-thin polymer film of uniform thickness. To cope with this, we modified the surfaces of carbon particles with a thin layer of a conductive polymer, by which carrier transport across the polymer layer be facilitated. The interior of TiO_2 mesopores, on the other hand, was filled with a redox-active ionic liquid as a fluid conductor. In order to realize such structure by coating of a single material on the TiO_2 mesopore, we have prepared a carbon-based soft composite material.

The material is highly electro-conductive and comprises polyaniline-loaded carbon black powders and an ionic liquid.

Published on the web (Advance View) March 14, 2007; doi:10.1246/cl.2007.480

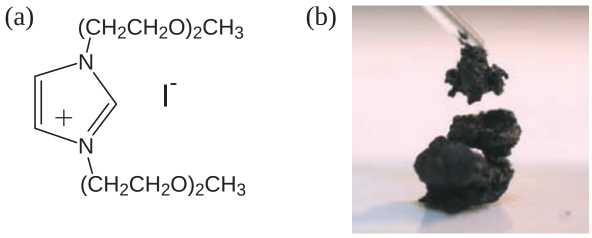

Figure 1. An example of 1,3-bis(ethyleneoxy)-type imidazolium iodide (EOI) (a); Polyaniline–carbon black conductive composite (PACB) material containing the above EOI compound (b).

It is prepared in the form of a hard incombustible paste and proved to be useful for solidifying the cell by simple coating processes.[35] The polyaniline-loaded carbon black (PACB) contains 20 wt % polyaniline emeraldine salt (half oxydized and hydrogenetaed polyaniline doped with organic sulfonic acid). An example for loading polyaniline on carbon black particles has been described by Sotzing et al.[36] To the PACB particle was added a hydrophilic ionic liquid, 1,3-bis(ethyleneoxy) derivative of imidazolium iodide (EOI), as shown in Figure 1a. A well-mixed dispersion of PACB of EOI (wt. ratio, 1:8.3) is a black paste as shown in Figure 1b, which is mostly solid having a clay-like high viscosity and is free of volatile components. A thick layer of the paste (90 µm) was sandwiched between the dye-sensitized TiO_2 layer and a FTO or metal counter-electrode. Here, the surface of counter-electrode is not treated for loading a catalyst (Pt, etc.) The soft PACB–EOI layer can get a good contact with the porous TiO_2 surface and flat counter-electrode, electrically bridging both surfaces, to form a solid-state photocell. This technique is also useful for making a full-plastic solid-state photocell based on our low-temperature TiO_2 coating methods.[13,29,30]

Figure 2 schematically shows how we improved the polymer-based DSC by using the carbon-based composite. Key aspects of the improvement are use of a soft composite layer to cover the porous surface and an ionic liquid to ensure electrical connection to the dye monolayer. In PACB, thickness of the polymer conductor is minimized, if not homogeneous, so that the hole injected at the surface of the polymer is immediately conveyed to carbon black with minimal loss in conduction. The bulk of carbon plays the roles of hole collector, counter-electrode, and cathode catalyst, simultaneously. Carbon black (CB)-coated counter-electrode has been applied to fabricate a high-efficiency DSC (9.1%), indicating excellent activity of porous CB as cathode.[37] At the junction of PACB and dyed TiO_2 surface, CB is placed very close to the dye monolayer separated by thin PA layer. Practically, a minimal distance forms between photoelectrode (TiO_2) and counter-electrode (carbon). Here, the role of polyaniline, n-type organic semiconductor, is to rectify the hole transfer, as a p-type conductor, at the interfaces of dye–PACB (solid–solid junction) and EOI–PACB (liquid–solid junction). This geometrical situation significantly reduces the internal resistance of the cell. In other words, the cell structure is characterized as having an extremely thin electrolyte layer, which only occupies the interior of mesopores. A similar idea has also been proposed by Kumara et al. to improve the performance of liquid-based DSCs.[38] Figure 3 depicts the structure of PACB-based solid-state DSC and the carrier-transfer processes across the mesoscopic junction. In the mesoscopic interior, where PACB is partially embedded, the imidazolium iodide, EOI, is electronically reducing (trapping hole from) the oxidized dye. The temporary produced oxidant, triiodide (or iodine), is immediately reduced in contact of PACB to reproduce EOI. This redox shuttle is considered to work with the absence of iodine as an initial additive to the EOI–PACB composite.

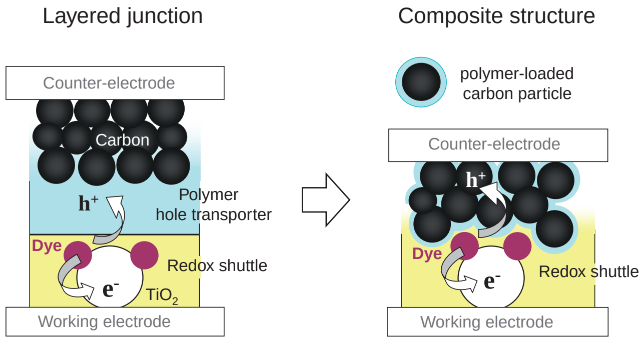

Figure 2. Experimental approach to the carbon-based solidification of a dye-sensitized photocell. The hole-conductive polymer as n-type semiconductor that rectifies carrier transport at the dyed TiO_2–carbon junction is incorporated in a multilayered structure (left)[34] and is hybridized with carbon particles to minimize the separation between dyed TiO_2 and the carbon counter-electrode (right).[35]

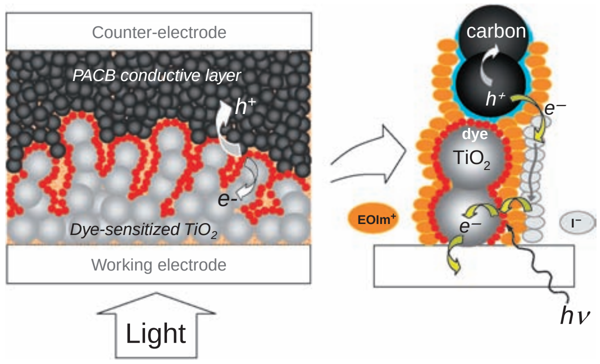

Figure 3. Structure of the PACB-based solid-state dye-sensitized solar cell and schematic illustration of the carrier transfer processes at the interfaces involving dye-adsorbed TiO_2, ionic liquid molecule, and PACB. $EOIm^+$ represents cation part of EOI.

Figure 4 displays photocurrent density–voltage (I–V) characteristics of the PACB-based photocell. By exposure to 1 sun intensity ($100\,mW\,cm^{-2}$), the cell produces a short-circuit photocurrent density (J_{sc}) of $12.8\,mA\,cm^{-2}$ and an open-circuit voltage (V_{oc}) of 0.56 V. Overall power conversion efficiency is 3.48%, which increases to 4.07% with a low photocurrent output at 1/4 sun intensity ($23\,mW\,cm^{-2}$). Figure 5 exhibits action spectrum of incident-photon-to-current quantum conversion efficiency (IPCE), which yields 48% at around 530 nm where the dye optical absorption takes a maximum. The IPCE obtained is still lower than those normally achieved by liquid electrolyte-based DSCs (>80%).[10] The main reason is assumed to be imperfect rectification of hole migration in the PACB–EOI composite. The role of polyaniline added to carbon is shown by its current rectification ability; A pure carbon black layer without polyaniline was found to work with much lower efficiency due to low fill factor.[35]

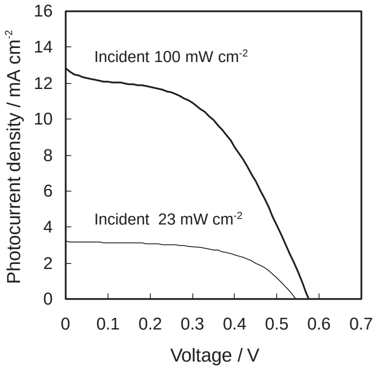

Figure 4. Photocurrent density–voltage (*I*–*V*) characteristics for the PACB-based solid-state dye-sensitized solar cell under incident intensities (AM 1.5) of 1 sun (100 mW cm^{-2}) and 1/4 sun (23 mW cm^{-2}).

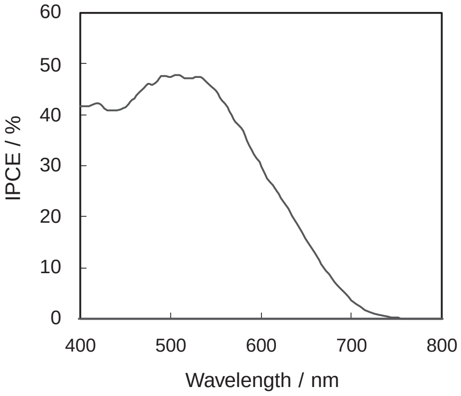

Figure 5. IPCE action spectrum of the PACB-based solid-state DSC.

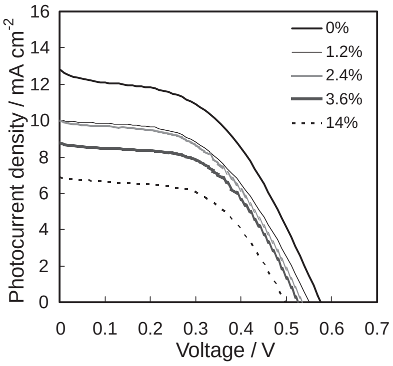

Figure 6. Effect of I_2 content (wt %) added to the PACB layer on the *I*–*V* characteristics. Irradiance, 100 mW cm^{-2}.

The efficiency obtained with PACB is amply high taking into account the simple way of cell making without cathode catalyst (Pt, etc.) and iodine. Important findings are that the addition of iodine to the EOI–PACB composite deteriorates the cell performance, as is demonstrated in Figure 6, and highest efficiency occurs by maximizing the PACB content in the composite. The former indicates that the redox shuttle inside the mesopore can work with EOI alone. This possibility is supported by the electron-exchange mechanism of carrier transfer related to triiodide/iodine redox system as has been studied by several groups.[6,39] Mixing of imidazolium iodide with oxide nanoparticles, such as TiO_2,[6] causes quasi-solidification of electrolyte, in which imidazolium cations densely adsorbed on TiO_2 creates a hopping route of the counter I^- along the array of cations without ionic diffusion. A similar phenomenon must take place when imidazolium iodide (EOI) incorporated in the mesopores being surrounded by TiO_2 surfaces, where a trace amount of iodine being produced by oxidation of EOI drives the electron conduction. The reason why the cell performance is maximized by increasing the PACB content is rationalized as that the latter increases the contact area of TiO_2–PACB, thus enhancing the hole transfer at the TiO_2–PACB interface.

The iodine-free solid-state DSC showed good durability of performance during long time preservation under ambient atmosphere and humidity even in the condition where sealing of the cell is omitted. The cell is stable even at high temperature (40–60 °C) because nothing is lost by evaporation and the solidified structure is fairly stable physically. Although high temperature accelerated tests are needed before finally assessing the cell lifetime, we are convinced of high stability and toughness of the cell.

♦ *Full-plastic Carbon-based Solar Cells*

Polymer–carbon composite is a cost-effective alternative to the conventional liquid electrolyte compositions comprising redox compounds, additives, and solvents. An extreme ease of fixing the electrodes is realized by using the paste-type conductor, which can be coated by screen printing. The quasi-solid paste works like an adhesive and puts together both electrodes by itself. Using the plastic electrode, cell-making processes can be further simplified by omitting high-temperature sintering for TiO_2 coating. Our low-temperature technologies for mesoporous TiO_2 preparation on ITO-coated polyethylene naphthalate (PEN) sheet (200-µm thickness and 13 ohm sq.$^{-1}$ resistance) have recently achieved a highest conversion efficiency of 6.4% using liquid triiodide/iodie-based electrolytes.[30] Key technology in this method is inter-connection of nano-particles by chemical dehydration condensation using aqueous titanium oxide sol. Figure 7 exhibits a TiO_2-coated ITO–PEN electrode for dye sensitization. This plastic electrode can be immediately combined with the soft carbon composite to devise a full plastic solid-state solar cell.

We have attempted various carbon-based composite materials to elicit high photovoltaic performance from dye-sensitized TiO_2-coated ITO–PEN electrodes.[40] The PACB–EOI composite yielded conversion efficiency less than 1%, which was unexpectedly low as the result of replacing the FTO glass with ITO–PEN. However, we found the cell performance is dramatically improved by selecting carbon nanotubes as conductors instead of using the polymer–carbon hybrid materials. Carbon nanotubes were mixed with EOI to give an iodine-free viscous paste for doctor-blade coating. On full-plastic cell fabrication using ITO–PEN films for working and counter-electrodes, photovoltage exceeding 0.6 V was obtained with multi-wall (MW) and single-wall (SW) carbon nanotubes (CNTs). Best efficiency is obtained with a very simple cell structure, in which an iodine-free composite of SW–CNT and EOI is made into junction with a mesoporous dyed TiO_2 surface. SWCNT has higher purity for

Table 1. Photovoltaic performances of ITO–PEN/dye–TiO_2/CNT–EOI/ITO–PEN solid-state plastic dye-sensitized photocells

Carbons	Light intensity	J_{sc}/mA cm^{-2}	V_{oc}/V	FF	η/%
SWCNT	1 sun	6.81	0.66	0.36	1.63
MWCNT	1 sun	4.33	0.60	0.39	1.01
SWCNT	1/4 sun	1.94	0.63	0.46	2.33

carbon content than MW–CNT and is known to possess metallic or semi-conductive property depending on the molecular structure of the tube, which differs from MWCNT that has less defined properties. Using a metal-coated plastic film as counter-electrode, thin full-plastic solid-state DSCs were constructed. Power conversion efficiency of the cell (effective area, 0.24 cm^2) reached 1.63% ($V_{oc} = 0.66$ V) under 100 mW cm^{-2} irradiance.[40] This flexible plastic cell gave a maximum IPCE of 30–35%. Table 1 shows the *I*–*V* performance parameters for SWCNT and MWCNT-based full plastic cells.

Figure 8 exhibits the thin body of the carbon-based full-plastic DSC. For this full-plastic cell, we can use various materials for counter-electrode, including ITO-coated plastic films (free of catalysts) and metal foils (Al, Cu, etc.). This variation becomes possible because no damage of the oxidant iodine is brought about. We also confirmed relatively high stability of the above full-plastic cell unless the flexible body is mechanically deformed.

◆ Photocapacitors as New Energy Devices

In the fields of energy storage devices, activated carbon (AC) having large surface areas (10^3 m g^{-1}) has been adopted for utility type capacitors of high charge–discharge capacity.[2,3] All kind of existing charge–discharge devices (condensers, capacitor, batteries, etc.) utilize electrochemical interfaces created by ionic electrolytes. The photo-generator, DSC, is also driven by electrochemical interfaces. In this viewpoint, we have invented a new type photovoltaic cell in which generation and storage abilities are combined in a single-layered structure of the cell. Historically, since the first invention of the silicon solar cell by Bell Telephone's group in 1954,[41] half a century of photovoltaic R & D has been spent to elevate the photoelectric efficiency.[42] Solar irradiation, however, is highly variable in time even in a sunny day. Apparently, users need secondary batteries which convert fluctuated energy into stable outputs of voltage and/or current. Photo-rechargeable device enables conversion of fluctuated light to stable electric energy. Such a new-type solar cell is highly sought after as the ubiquitous solar power not depending on the use of an additional storage cell. In this respect, efforts have been made to combine a photovoltaic electrode and redox-active materials for rechargeable reactions.[43–45] Repeated oxidations and reductions, however, shorten the lifetime of the cell. The capacitor is a more desirable tool for its long lifetime due to redox-free electrolytes and for rapid response to current change (light variation).

A photo-charging type capacitor, which we have developed and named the photocapacitor,[46] converts and stores, simultaneously, the visible light absorbed by a dye-sensitized nanocrystalline semiconductor. The device is a simple sandwich-type cell consisting of a light-absorbing photoelectrode, a redox-free liquid electrolyte, and a counter-electrode. The photoelectrode consists of a heterojunction of dyed semiconductor nano-particles and activated carbon (AC) particles and counter-electrode bears a porous AC layer. In principle, charging reaction is initiated by the dye-sensitized electron injection to semiconductor layer at the heterojunction interface. After this charge separation, electrons flow via external circuit to AC layer of the counter-electrode. Photo-generated holes of the dye transfer to the AC layer of photoelectrode. Positive charges (holes) and negative charges (electrons) are ultimately accumulated on the microporous surface of AC that holds the electric double layer in contact with a liquid electrolyte of high ionic concentration. Photocapacitor does not use any redox system in electrolyte. Its simple device structure and carrier-transport mechanisms are displayed in Figure 9. Here, the softness of AC-containing conductive layer helps to ensure the electrical junction of AC with the rough surface of TiO_2.

AC-coated dye–TiO_2 layer was prepared on FTO glass substrate. According to the practice of the solid-state DSC, we must fill the interior of N719-adsorbed TiO_2 mesopores with some hole conductor that can be introduced in a liquid form. Because AC layer is to be soaked by a liquid electrolyte, ionic liquid, which can diffuse to the electrolyte, is not a good choice as a redox shuttle. Instead, we employed LiI as a solid-state ionic conductor that fills the pore. A solution of LiI in acetonitrile was added to the dyed TiO_2 mesopore. After repeated drying, the interior TiO_2 surface is filled with LiI (0.2 mg cm^{-2}). The AC layer is immobilized on the top of TiO_2 layer by casting a liquid suspension containing AC (surface area, 1200 m^2 g^{-1}) and polyvinylidene fluoride as a binding material in *N*,*N*-dimethylformamide and drying the resulting film at 60 °C for 50 min. The photoactive layer thus obtained is a stack of a thin LiI-incorporated mesoporous TiO_2 film and a thick AC layer (200–300 μm) with their interface bearing the dye monolayer. Counter-electrode is combined with the photoelectrode by insertion of a porous resin film as a separator to avoid short circuit. The AC layers and the porous separator are soaked with an electrolyte solution, which is, typically, propylene carbonate containing 15 wt % $(CH_3CH_2)_4NBF_4$. Although organic electrolytes have been generally used for their high stability against electrochemical polarization (stable up to 2.5 V), they are not necessarily required for our device since photo-generated voltage is of a low range less than 1 V. Desirable electrolytes in this respect would be aqueous electrolytes capable of high coulombic capacity. The iodine-free electrolyte allows us to use various kinds of cheep metals such as Al and Cu as electrode substrates.

Charging of the photocapacitor is done by visible light irradiation to the photoelectrode in the condition of short-circuiting the external circuit. Charging current (photocurrent) in the photocapacitor is fully dependent on the light intensity and tends to decrease with time until charging is saturated. In discharge, current density was regulated as constant by galvanostatic circuitry. The latter operation allows assessment of the cell capacitance. Figure 10 shows the results of photo-charge and discharge characteristics of the photocapacitor, where the device was illuminated with white light of 100 mW cm^{-2}. The illuminated cell develops a negative photovoltage at around −0.6 V vs the counter-electrode, which serves itself as a driving force for

Figure 7. Mesoporous TiO_2-coated ITO–PEN film as working electrode for dye-sensitization. The TiO_2 layer shows high hardness against writing by pencil (upper) and ball-point pen (lower). Electrode thickness, 210 µm including 10 µm-thick TiO_2 layer.

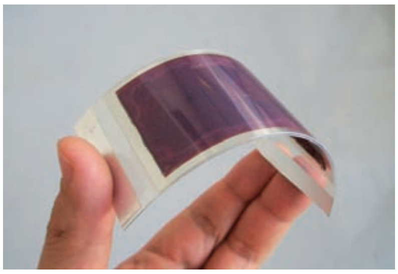

Figure 8. Thin flexible body of carbon-based solid-state full-plastic DSC (device thickness, around 450 µm) constructed on ITO–PEN films.

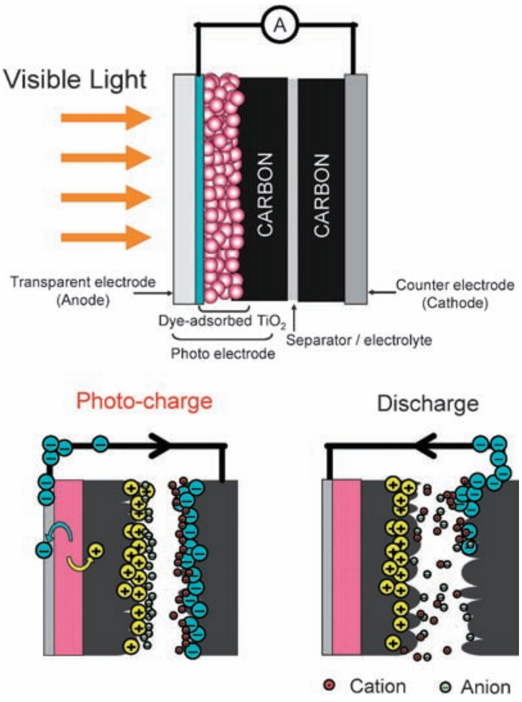

Figure 9. Two-electrode sandwich-type structure of the carbon-incorporated photocapacitor (upper) and charge-transfer mechanism in the processes of photo-charging and discharging (lower).

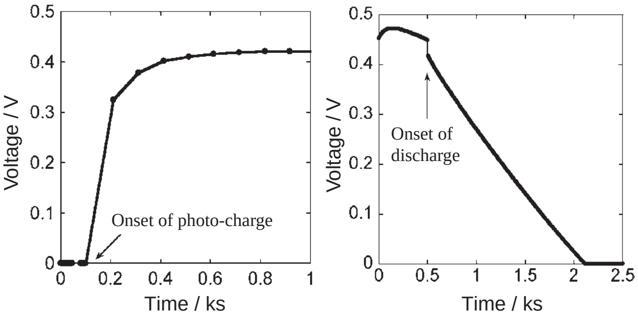

Figure 10. Characteristics of photo-charge (left) and discharge (right) at the photocapacitor in terms of voltage change with time. Charge and discharge are conducted with a constant incident intensity ($100\,mA\,cm^{-2}$) and a constant current density ($47\,\mu A\,cm^{-2}$), respectively. This flat device yielded a capacitance per area of $0.69\,F\,cm^{-2}$.

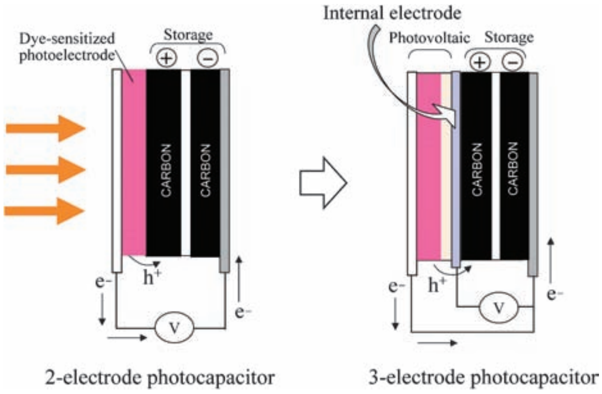

Figure 11. Three-electrode-type photocapacitor is an improved version of the basic two-electrode type by introducing an internal bi-functional electrode working as cathode of the photovoltaic cell and anode of the storage cell, achieving high charging voltage.

self-charging reaction. The charged photoelectrode showed +0.1 V vs counter-electrode, indicating that a negative charge (electrons) was stored on the counter-electrode side. On discharge, cell voltage exhibited a constant decrease with time, accompanied by an initial IR drop due to the cell resistance. This linear decrease of voltage is a characteristic of the double-layer capacitor,[3] with which the value of capacitance is determined by the reciprocal of the slope, $I\Delta t/\Delta V$, where I and t represent current and discharging time, respectively. Concerning the role of LiI in the mesoporous interior, photo-produced holes of the dye are assumed to react with LiI as a hole trapping agent to regenerate the dye; Dye (hole) + LiI → Dye + Li^+ + $1/2I_2$. The product, I_2, simultaneously can react with adjacent AC undergoing electronic reduction to regenerate LiI. It is known that both I^- and I_2 strongly interact with AC by adsorbing on its microporous surface.

Photocapacitor achieves simultaneous conversion and storage of light energy exhibiting an open-circuit voltage >0.45 V and a charge capacity per area of $354\,mC\,cm^{-2}$. The turnover number of the dye (>25) in photo-charging indicates that a major portion of dye holes transfers to the bulk of the AC without remaining at the dye molecule. The device exhibits a capacitance of 0.69 F cm^{-2} with respect to the area of dye-sensitized photoelectrode. A key subject for performance is to elevate the charging voltage because 0.45 V is much behind the maximal photovoltage of DSC (around 0.8 V). This is apparently influenced by the presence of a space charge Schottkey barrier at $\mathrm{TiO_2}$ that can intervene the electron transfer for discharge process. To overcome this, we have designed a three-electrode type photocapacitor, in which an internal electrode is inserted between photo- and counter-electrodes, which functions on its both sides as the cathode of photoelectrode and the anode of capacitor, simultaneously.[47] Three-electrode configuration for rechargeable photocells has been formerly shown by Segawa and Nagai, who invented a redox-type photo-rechargeable cell using doped polypyrrole as a storage material.[48] Figure 11 illustrates our method of inserting the additional bi-functional internal electrode in the photocapacitor. The internal electrode can be a thin flexible metal foil. In this cell configuration, photoelectric generation unit and storage unit are physically separated and operations of charge and discharge are switched by external circuit. We could obtain high charging voltage exceeding 0.8 V with a charging capacity of 1.12 C cm^{-2}. The device showed excellent cycleability for repeated photo-charge and discharge, corroborating high stability of the carbon-based electrochemical cell.

A merit of the three-electrode configuration is that photovoltaic unit and storage unit can be independently optimized by changing the materials to maximize the performance. Use of triiodine/iodide-based organic electrolytes capable of high-density photocurrent can maximize the photocharging rate. At the moment of this contribution, three-electrode photocapacitor reached a charging voltage of 0.85 V yielding a capacitance per the amount of AC of 200 F g^{-1} (6.6 F cm^{-2}) and energy density per area of 230 μW h cm^{-2}. Further, we have confirmed that the global solar energy storage efficiency starting from the conversion of incident energy and ending with energy storage in the cell is reaching more than 4%. This performance is backed by a compact layered structure of the cell that eliminates an electrical loss of connecting photovoltaic and storage cells after current collection and by wiring.

A goal of this study is to construct a thin layer cell by which influence of light variation is minimized in the electric power output. Photocapacitor thereby works as the solar cell endowed with power-stabilizing function against light variation, the function being incorporated at the material level in a single device. Figure 12 is the data demonstrating the ability of the photocapacitor in stabilizing the power output under exposure to random fluctuation of outdoor sunlight. This result shows the feasibility of designing a stable solar power generator by reinforcing the storage function of the cell. Finally, the structure of photocapacitor is immediately converted to a thin flexible devices using $\mathrm{TiO_2}$-coated plastic electrodes.[13,30]

◆ Outlooks toward Printable Electronics

Potential applications of carbon-based soft conductors were described for designing solid-state photoelectrochemical devices. Carbons are elecrtrochemically stable and highly cost-effective. By tayloring the interface of nano-carbons and partner organic or inorganic materials, electrochemical interfaces can be solidified holding the rectifying ability for current production. Preparation of printable composite pastes forming such solidified interfaces creates new technologies for low-cost organic electronic devices. We would like to stress the usefulness of the printable electrode materials in the current rapidly growing fields of plastic electronics and printable electronics.[49,50] Combination of the printable electrode materials and plastic substrates realizes lightweight flexible devices, which are environmentally benign in materials and their vacuum-free manufacture processes. The industrial applications for flexible photovoltaic devices are enormous in consumer electronics including electronic books, cell phones, personal digital assistants (PDAs), etc., which need suitable lightweight ubiquitous power. To this end, we are concentrating on developing vacuum-free and low-temperature coating methods for electrode fabrication.

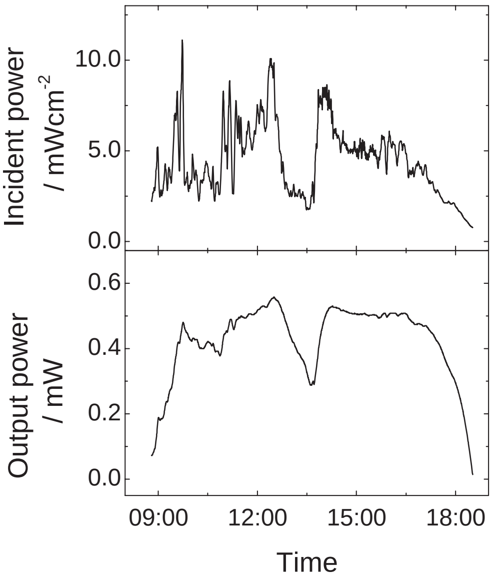

Figure 12. A profile of output electric power at the three-electrode-type photocapacitor (lower diagram) under exposure to fluctuating outdoor sunlight (upper diagram). The time course of output power change is stabilized in amplitude compared to the incident sunlight energy that frequently and largely varies.

The studies presented here were supported by a Grant-in-Aid for Scientific Research on Priority Areas (417) from the Ministry of Education, Culture, Sports, Science and Technology, New Energy and Industrial Technology Development Organization (NEDO), and Japan Science and Technology Agency (JST). The authors thank Dr. M. Ikegami of Toin University of Yokohama for discussions of dye-sensitized electrodes.

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