

Photo-Charging Process in a Photo-Rechargeable Battery with Composite Electrodes of TiO₂ and Carbon Fibers

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The photo-charging process of composite electrodes of TiO₂ and carbon fibers (CFs) was studied for a photo-rechargeable battery in which photon energy can be converted to electrochemical energy and *in-situ* stored. The electrodes were prepared by sintering CFs which had been applied with TiCl₄ diluted by acetone. Several perchlorate electrolytes containing Li⁺, K⁺ or Pb²⁺ and CFs with different structures of carbon were used. Experimental results showed that Li-ions in electrolytes only contributed to the photo-charging and that the discharge current of an electrode using disordered carbon like CFs was larger than that using graphite like CFs. The results suggested that photo-charging was done by the formation of lithiated carbon at sites of disordered carbon such as the edges of graphite crystallite and the defects of aromatic ring.

Key words: photo-rechargeable battery, titanium oxide, carbon fibers, solar device

1. INTRODUCTION

A photo-rechargeable battery (PRB) is a new solar device that converts photon energy to electrochemical energy and *in situ* storages it. It has an advantage to utilize solar energy in dark without any external batteries. The concept of PRB based on a photo-induced intercalation phenomenon was suggested by Tributsch in 1980.¹⁾

The electrode of PRB has two functions of the opto-electric conversion of absorbed sunlight and the storage of electric energy by reversible intercalation. For the practical use, the electrode must be chemically stable in electrolyte under the irradiation. However, any materials good for the practical use have not been found yet, while many layered semiconducting materials¹⁻⁵⁾ and semiconducting polymers⁶⁻⁸⁾ were investigated for the electrode. One of the reasons exists in the difficulty to optimize the two functions with single material which is chemically stable.

We have proposed a composite electrode^{9,10)} in which the two functions of the opto-electric conversion and the storage are attributed to different materials. Such composite electrode has advantages in optimizing physical properties of each substance separately. In

this study, a semiconducting photocatalyst of TiO₂ and a layered material of carbon fibers (CFs) are used for the opto-electric conversion and the storage, respectively. The photo-rechargeable properties are tested by using TiO₂/CFs composite electrode.¹¹⁾ So far, it was confirmed that the TiO₂/CFs electrode had photo-rechargeability.

In this paper, the photo-charged quantities of TiO₂/CFs electrode were measured with different perchlorate electrolytes containing Li⁺, K⁺ or Pb²⁺ ions in order to find active cation in the photo-charging process. Furthermore, four types of CFs with different carbon structure were tested to find the suitable structure of carbon to storage the active cations in CFs.

2. EXPERIMENTAL

Four types of CFs used for electrodes are shown in Table I. The CFs made with the precursor of meso-phase pitch have large graphitic crystallites. Furthermore, the crystallites containing of disordered graphite-like structure are graphitized by a heat treatment.

The composite electrodes of TiO₂/CFs were prepared by sintering CFs which had been applied

Table I. Four types of CFs used for electrodes.

	Precursor	Heat treatment	Size of crystallites	Graphitization degree of crystallites	Maker
HT-MPP	meso-phase pitch	○	large	high	Nippon Sekiyu Co.
MPP	meso-phase pitch	×	large	low	Nippon Steel Co.
HT-PAN	polyacrylonitrile	○	small	high	Toho Rayon Co.
PAN	polyacrylonitrile	×	small	low	Asahi Carbon Co.

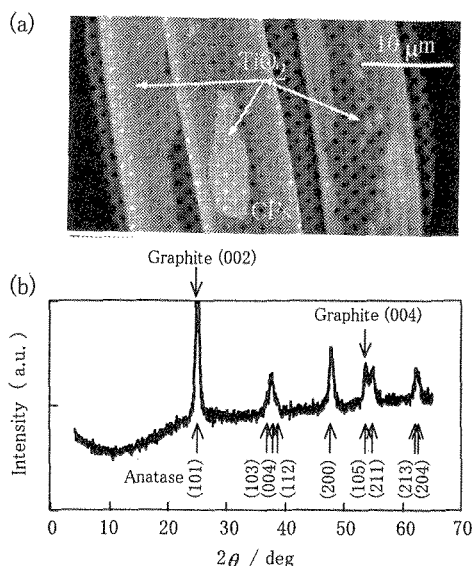


Fig. 1 SEM image and X-ray diffraction pattern of TiO_2/CFs (HT-MPP) electrode.

with titanium tetrachloride acetonitrile dilute solution at 500°C in air for 2 hours. To remove the residue and unsticking fragments of TiO_2 , the composite electrodes were washed in acetone by an ultrasonic washing machine.

Figure 1(a) shows a SEM image of TiO_2/CFs (HT-MPP) electrode. It is found that each filament of CFs is partially covered by thin layers of TiO_2 . The thickness of the layer is estimated to be much less than $1\ \mu\text{m}$ compared with the diameter of filaments of $10\ \mu\text{m}$. From the X-ray diffraction pattern of TiO_2/CFs (HT-MPP) electrode shown in Fig.1 (b), TiO_2 layers are confirmed to have an anatase-type crystal structure.

Figure 2 shows a diagrammatic sketch of the working electrode (WE) using TiO_2/CFs and the measurement configuration of three-electrode cell with the electrolyte of perchlorate acetonitrile solution $0.5\ \text{mol dm}^{-3}$. The cation in the electrolyte was selected to be Li^+ , $\text{Li}^+ + \text{K}^+$ (1:1) or Pb^{2+} . A bundle of CFs and a Pt-wire of 1 mm diameter were used for a counter electrode (CE) and a reference electrode (RE), respectively. The WE was irradiated by a xenon short

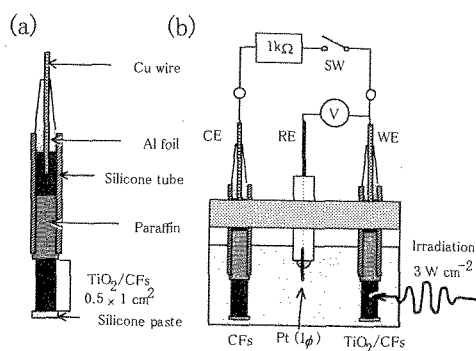


Fig. 2 Diagrammatic sketch of working electrode and the measurement configuration of three-electrode cell.

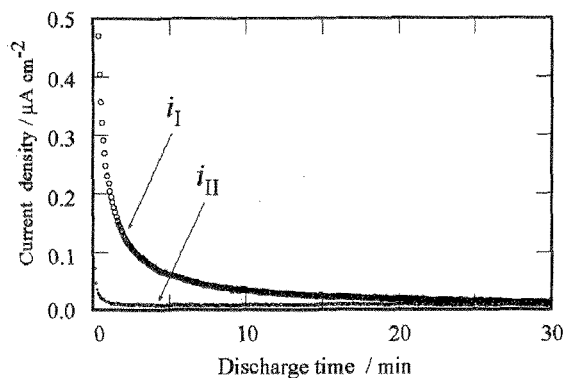


Fig. 3 Discharge currents i_I and i_{II} of TiO_2/CFs (HT-MPP) electrode

arc lamp of $3\ \text{W cm}^{-2}$.

The photo-rechargeability was estimated from the photo-charged quantity measured by the following procedures; 1) irradiation of WE for 15 min with opening WE-CE, 2) leaving WE in the dark for 1 min, 3) measurement of discharge current of i_I for 30 min with connecting WE and CE by a load of $1\ \text{k}\Omega$. For comparison, the discharge current i_{II} was measured without irradiation with the same procedure as i_I . The procedure was repeated until the profiles of i_I and i_{II} does not change. The discharge currents measured for a TiO_2/CFs (HT-MPP) electrode are shown in Fig. 3 where the direction of the current from WE to CE is taken to be positive. Thus, the photo-charged quantity per electrode weight w is defined by

$$Q_{\text{ph}} = \frac{1}{w} \int (i_I - i_{II}) dt. \quad (1)$$

3. RESULTS AND DISCUSSION

3.1 Cation dependence of Q_{ph}

Table II shows the variation of Q_{ph} measured for a TiO_2/CFs (HT-MPP) electrode in electrolyte containing different cations. It is found that the value of Q_{ph} is almost proportional to the amount of Li^+ . The result suggests that Li^+ -ions contribute to the photo-charge.

Figure 4 shows the variation of the potential of WE against RE with and without irradiation. Here, TiO_2/CFs (HT-MPP) electrode was used for WE in $\text{LiClO}_4\ 0.5\ \text{mol dm}^{-3}$ acetonitrile

Table II. Q_{ph} of TiO_2/CFs (HT-MPP) electrode in electrolyte of different cations.

Cation	$Q_{\text{ph}} / \text{mC g}^{-1}$
Li^+	11.2
$\text{Li}^+ + \text{K}^+$ (1:1)	5.95
Pb^{2+}	1.45

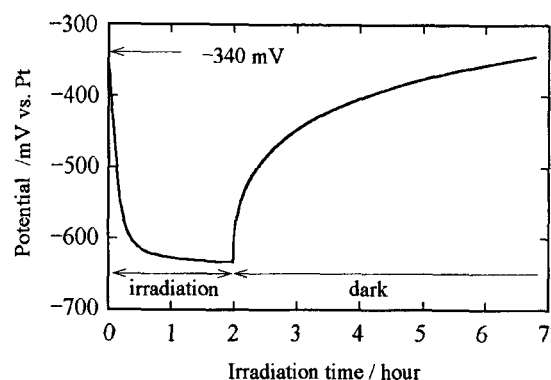
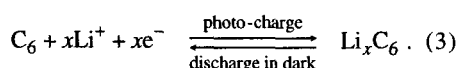
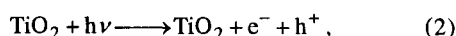


Fig. 4 Potential variation of $\text{TiO}_2/\text{CFs}(\text{HT-MPP})$ electrode with and without irradiation.

solution. With irradiation, the potential dropped by 300 mV from the rest potential of -340 mV and saturated to a value in about 2 hours. The potential drop is caused by a separation to electron-hole pairs with a photo excitation in the TiO_2 layer. From the direction of the potential variation due to the irradiation, the electrons are considered to move inside the CFs, the holes to the surface of TiO_2 layers.

Since the discharge current i_1 is in the anodic direction as was mentioned above, the electrons moved inside the CFs are considered to be stored by the formation of lithiated carbon of Li_xC_6 . Thus, the reaction in the photo-charging process is written as



3.2 Formation of lithiated carbon

Table III shows the values of Q_{ph} for different types of CFs in LiClO_4 0.5 mol dm^{-3} acetonitrile solution. The value of Q_{ph} was larger for polyacrylonitrile (PAN) based CFs than for meso-phase pitch (MPP) based ones, and the value of Q_{ph} was larger for non-heat treated CFs than for graphitized-heat treated ones. Since the structure of CFs is changed by a precursor and a graphitized-heat treatment as shown in

Table III. Q_{ph} for different kinds of CFs.

CFs	$Q_{\text{ph}} / \text{mC g}^{-1}$
HT-MPP	11.2
MPP	14.5
HT-PAN	43.0
PAN	66.7

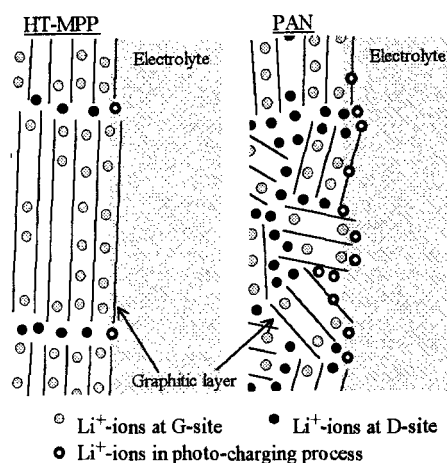


Fig. 5 Formation of lithiated carbon in photo-charging process.

Table I, the formation of lithiated carbon in the photo-charging process is considered to be influenced by the structure of CFs.

The relation between the structure and the formation of lithiated carbon has been investigated in detail for Li-ion secondary batteries.¹²⁻¹⁴ The formation of lithiated carbons is classified into following two types: 1) the intercalation of Li^+ -ions into interlayer sites of graphite (G-site), 2) the formation of lithiated carbon at disordered carbon sites (D-site) such as the edges of graphitic crystallite or the defects of aromatic rings of graphite.

The model for the formation of lithiated carbon on HT-MPP and PAN is shown in Fig. 5. As shown in the figure, PAN has a lot of D-sites because the graphitic crystallites are small and have many defects. On the contrary, HT-MPP has small number of D-sites due to its precursor and heat treatment. Therefore, it is considered that the value of Q_{ph} depends on the number of D-sites, and that the formation of lithiated carbons at D-sites contributes to the photo-charge.

The activation energy necessary for the formation of lithiated carbons at D-sites must be distributed in a wide range because Li^+ -ions are considered to bond with various carbons at defects and the edge of crystallites. Although it is difficult to estimate the activation energy caused by the irradiation, the energy should be very small. This is because the photo-charged quantity was much smaller than the value when every G-sites were assumed to contribute to the charge, and the D-sites near the surface of CFs must have low activation energy for the formation of lithiated carbons.

4. CONCLUSIONS

From the photo-charged quantities of TiO₂/CFs electrodes with several perchlorate electrolytes containing Li⁺, K⁺ or Pb²⁺ ions, it was found that Li⁺ -ions contribute to photo-charge. The reaction formulas for the photo-charging process with Li⁺ -ions were suggested from the potential variation under irradiation and the profile of discharge current. The experimental results of photo-charged quantities with different kinds of CFs suggested that disordered carbon was suitable for the electrode material of photo-rechargeable battery and that the formation of lithiated carbon at sites of disordered carbon such as the edges of graphite crystallites and the defects in aromatic rings contribute to the photo-charge.

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