Photovoltaic lithium-ion battery fabricated by molecular precursor method

Hiroki Nagai*, Tatsuya Suzuki[†], Yoshihisa Takahashi[†] and Mitsunobu Sato^{*‡}

**Department of Applied Physics, School of Advanced Engineering
Kogakuin University, 2665-1 Nakano, Hachioji, Tokyo, Japan*

*[†]Applied Chemistry and Chemical Engineering Program, Graduate School
Kogakuin University, 2665-1 Nakano, Hachioji, Tokyo, Japan*

[‡]lccsato@cc.kogakuin.ac.jp

Received 11 March 2016; Accepted 17 April 2015; Published 16 June 2016

A novel thin-film lithium-ion battery (LIB) which can be charged by the light irradiation was fabricated by molecular precursor method. The unprecedented, translucent thin-film LIB, fabricated on a fluorine-doped tin oxide pre-coated glass substrate, was attained by using the active materials, titania for anode and LiCoO_2 for cathode, respectively. The averaged potential at 2.04 V was observed by applying a constant current of 0.2 mA. Then, that at 1.82 V was detected after 60 s during the sequential self-discharge process. The charging voltage of the assembled battery was 1.38 V with irradiation of 1-sun, the self-discharge voltage was 1.37 V. Based on the calibration curve of the charging voltages over constant currents ranging from 0–1.0 mA, the detected value can be theoretically reduced to the charging operation by applying a constant current of approximately 60 μA . The charge and discharge of this device was stable voltage at least 30 cycles. The two-in-one device can simultaneously generate and store electricity from solar light, the renewable energy source, and may be applied in smart windows for distributed power system according to on-site demand.

Keywords: Photovoltaic device; lithium-ion batteries; translucent; molecular precursor method; thin film.

Distributed power generation using renewable energy sources, such as solar light, can efficiently supply electricity according to on-site demand. If the electrodes of lithium-ion batteries (LIBs), which are the dominant power sources for most portable electronics, could function as a solar cell, the storage device could provide electricity without an electric power supply.

We recently reported a transparent thin-film device that can function as a LIB. The thin-film LIB was fabricated with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) for the anode and $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ (LFP) for the cathode on a fluorine-doped tin oxide (FTO) pre-coated glass substrate, and an electrolytic solution dissolving LiPF_6 . A wet process known as the molecular precursor method (MPM) was used to fabricate the active material thin-films with thicknesses of 100 nm on the substrates.¹ In the charge/discharge cyclic test of the LIB assembled with these electrodes, the synchronous electrochromic reactions of the LTO were clearly observed during repeated operation. Therefore, the transparent thin-film LIB has many practical applications, such as monitoring electrochemical reactions and use in electrochromic windows.

Zhang *et al.* reported that titania particles immobilized on an anodic electrode constitute an excellent candidate for LIB active materials because of their high safety, good capacity retention, and low self-discharge.² In fact, titania has excellent cyclability and chemical stability and negligible toxicity in LIBs.^{3,4} Additionally, anatase nanotubes have also been characterised as active materials and have been shown to have electrochemical potentials of 1.5–1.7 V versus Li/Li^+ .⁵ Regarding the chemical fabrication of two-in-one LIBs, we are therefore interested in the photovoltaic nature of LIBs including transparent thin films of titania on their anodes because we previously fabricated both a transparent photocatalytic titania thin film and the abovementioned LIB using the MPM, which was mainly developed in our prior study.⁶ The MPM used to fabricate the active materials is a wet process that can be used to produce thin films of various metal oxides or phosphates, including titania with high photoreactivity, Cu_2O as a *p*-type semiconductor, and biocompatible calcium phosphate compounds.^{7–9} This method is based on the inclusion of metal complexes in coating

[‡]Corresponding author.

This is an Open Access article published by World Scientific Publishing Company. It is distributed under the terms of the Creative Commons Attribution 4.0 (CC-BY) License. Further distribution of this work is permitted, provided the original work is properly cited.

solutions, which have many practical advantages, such as excellent stability, homogeneity, miscibility, and coatability. This is because highly stable metal complexes can be dissolved in suitable solvents, such as ethanol, after being combined with appropriate alkylamines. Furthermore, the resultant solutions can form excellent precursor films through various coating procedures, including the spin-coating method. A uniform thin film can be easily obtained by heat treating the precursor film according to the stoichiometric quantities of the metal complexes in the precursor solution.

In the present study, the precursor films of the titania and LiCoO₂ thin films were formed using a spin-coating method with the commercially available, newly prepared precursor solution at ambient temperature to fabricate the active materials on the FTO pre-coated glass substrate. The anode and cathode with the titania and LiCoO₂ thin films were obtained facilely by heat treating the precursor films in air.

CH₃COOLi · 2H₂O was purchased from Kanto Chemical Co., Inc., Japan (CH₃COO)₂Co · 4H₂O, TiO₂ molecular precursor solutions (Ti⁴⁺ = 0.5 mmol g⁻¹), and butylamine were purchased from Wako Pure Chemical Industries, Ltd., Japan. Ethanol was purchased from Ueno Chemical Industries, Ltd., Japan and was dried on 4A molecular sieves before use. Other materials were used without further purification. Celgard 2400 was used as the separator. The electrolyte solution was 1-M LiPF₆ in ethylene carbonate/dimethyl carbonate/diethylene carbonate (1:1:1 by weight, DANVEC, China). FTO pre-coated soda lime glass substrates were purchased from Asahi Glass Co., Ltd., Japan. Glass substrates with dimensions of 20 × 33 × 1.8 mm³ were used. Double-coated adhesive polyester tape, which was used as a spacer between the electrodes, was purchased from Nitto Denko, Corp., Japan.

The LiCoO₂ precursor solution was prepared by mixing 0.51 g of the lithium oxide precursor solution and 0.51 g of the cobalt oxide precursor solution. The mixed solution was stirred at ambient temperature for 20 min. Then, 0.16 g of 4A molecular sieves was added to the solution. The lithium oxide precursor solution was obtained as follows: 0.64 g (6.2 mmol) of CH₃COOLi · 2H₂O and 1.83 g (25.0 mmol) of butylamine were added to 10 g of ethanol. The solution was stirred at ambient temperature for 1 h. The concentration of Li⁺ ions was 0.50 mmol g⁻¹. Then, 0.12 g of 4A molecular sieves was added to the solution. The cobalt oxide precursor solution was obtained as follows: 1.90 g (7.62 mmol) of (CH₃COO)₂Co · 4H₂O and 3.35 g (45.7 mmol) of butylamine were added to 10 g of ethanol. The solution was stirred at ambient temperature for 1 h. The concentration of Co²⁺ ions was 0.50 mmol g⁻¹. Then, 0.28 g of 4A molecular sieves was added to the precursor solution.

Precursor films of TiO₂ and LiCoO₂ on the FTO pre-coated glass substrate were formed via a spin-coating method

at ambient temperature using a two-step process: the first step was carried out at 500 rpm for 5 s, and the second was performed at 2000 rpm for 30 s. The precursor solutions (50 μL) were dropped using a micropipette and spin-coated on a 20 × 20 mm² area of the substrate. The precursor films were pre-heated in a drying oven at 70°C for 10 min. Then, the precursor films of TiO₂ and LiCoO₂ were heat treated for 30 min at 500°C and at 550°C, respectively, in air.

The crystal phase of the heat-treated thin films adhered onto the FTO glass was examined using a MXP-18AHF22 (Bruker AXS, USA) X-ray diffractometer with Cu Kα radiation generated at 45 kV and 100 mA. The parallel beam optics with an incident angle of 0.25° in the 2θ range of 10–50° was used in each measurement. The thickness of each film was measured by a stylus profilometer (DEKTAK-3, Sloan, USA). The transmittance spectra of the assembled battery were measured in the wavelength range of 300–1100 nm using a UV-3600 spectrophotometer (Shimadzu Corp., Japan) in double-beam mode; air was used as the reference.

The thin-film LIB was assembled according to a recently reported procedure.¹ The charge/discharge cyclic test of the assembled battery was performed using a DC voltage monitor VOAC7523H (Iwatsu electric Co., Ltd., Japan) in two different modes.

In the typical current-insertion mode, the charging test of the assembled battery was measured by providing the constant current of 0.2 mA using a DC voltage source/monitor (6241A, ADC Co., Ltd., Japan). The charge and self-discharge cycle was repeated to times at 60 s intervals at room temperature.

In the light-irradiation mode, the charging test of the assembled battery was performed under 1-sun irradiation using a solar simulator (Lax-Cute, Asahi spectra, Japan), and the voltage was measured with the abovementioned monitor. The irradiated area of the battery was 4.0 cm². The repeated charge and self-discharge test of the assembled battery was performed sequentially under light irradiation 30 times at 60 s intervals.

A conventional three-electrode system was used for the current density measurements: TiO₂ and LiCoO₂ thin films on the FTO pre-coated glass substrate were used as the working electrode. A Cu wire was attached to the FTO pre-coated glass substrate by carbon tape. For all cases, a Pt metal plate that was equal in size to the working electrode, and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively. The current density of the sample electrodes was recorded at 10 s intervals for 30 min using a potentiostat/galvanostat (VersaSTAT 4, Princeton Applied Research, USA) under natural potential and both in the dark and under 1-sun irradiation from a solar simulator. All measurements were performed in a 0.1 M Na₂SO₄ solution after bubbling Ar gas at 50 mL min⁻¹ for 10 min.

Fig. 1. XRD patterns of (a) TiO_2 and (b) LiCoO_2 on the FTO pre-coated glass substrate with thicknesses of 110 nm and 80 nm, respectively. The peaks are denoted as follows: ∇ — TiO_2 , $\diamond$ — LiCoO_2 , $\circ$ — FTO, $|$ — unknown.

The X-ray diffraction (XRD) pattern of the thin film that had a thickness of 110 nm and was fabricated by heat treating the titania precursor film is shown in Fig. 1(a). The peaks at $2\theta = 25.40^\circ$ and 48.30° are assignable to the (101) and (200) phases, respectively, of the anatase structure of titania (JCPDS Card 21-1272). The other peaks observed in the pattern could be ascribed to the FTO (JCPDS Card 41-1445), although several peaks with very small intensities could not be assigned. The XRD pattern of the thin film that had a thickness of 80 nm and was fabricated by heat treating the LiCoO_2 precursor film is shown in Fig. 1(b). The peaks at $2\theta = 19.05^\circ$, 37.30° , and 45.50° can be assigned to the (003), (101), and (104) phases, respectively, of LiCoO_2 (JCPDS Card 44-145). Additionally, peaks that could be ascribed to the FTO and several unassignable peaks at positions identical to those noted in the abovementioned titania thin film were observed.

Because the expected active materials could be obtained, the thin-film device was assembled according to the procedure we recently described for fabricating transparent LIBs.¹ The transmittance spectra of the newly assembled device are shown in Fig. 2. The optical transmittance of the device was 50%, which was observed at 700 nm, the lowest value in the visible region, and the device is clearly translucent. A typical charge/discharge cyclic test was performed with a DC voltage source/monitor and was repeated 30 times at 60 s intervals. The averaged potential at 2.04 V was observed by applying a constant current of 0.2 mA. Then, that at 1.82 V was detected after 60 s during the sequential self-discharge process (Fig. 3a).

TiO_2 has been considered to be a good alternative to graphite anodes for conventional LIBs because of its appropriate discharge plateau potential in the range of 1.50–1.75 V

versus Li/Li^+ , which would decompose organic electrolytes.^{4,10} In addition, the layered structure of LiCoO_2 is chemically and electrochemically stable and exhibits a relatively high capacity of approximately 140 mAh g^{-1} and a discharge plateau potential of 3.8 V versus Li/Li^+ .¹¹ Based on these plateau values, the potential difference between TiO_2 and LiCoO_2 can be theoretically estimated in the range of 2.3–2.0 V. Therefore, a device constructed of these active materials on a FTO pre-coated glass substrate could be operated as a typical LIB because the detected potentials in the charge/discharge cycles are in good agreement with the theoretical values. Therefore, the lithium intercalation/de-intercalation reactions in the active materials can be written as:

The repeated charge and self-discharge test of the LIBs performed here study was also conducted under light irradiation and in the dark with no electrical supply 30 times at 60 s intervals. The 1-sun irradiation was achieved using a solar simulator and monitoring with a DC voltage monitor. The irradiated area of the LIB was 4.0 cm^2 . The voltage change during the test is shown in Fig. 3(b). The averaged voltages were 1.32 V during 1-sun irradiation and 1.29 V in the dark during the self-discharge process. In Fig. 3(b), a time required to stabilize at 1.32 V was observed. In the case of continuous irradiation to the device under the identical conditions in the exception of the 60 s intervals, the charging voltage reached 1.32 V after 6 min.

Additionally, the repeated charge and self-discharge test of this photovoltaic LIB, which was charged once for 20 s by providing a current of 1.0 mA, was performed under light

Fig. 2. Transmittance spectrum of the assembled battery.

Fig. 3. The charge/discharge cyclic test of the assembled battery with (a) a constant current of 0.2 mA (black line), (b) 1-sun irradiation (blue line), and (c) 1-sun irradiation after providing a constant current of 1.0 mA (red line).

irradiation 30 times at 60 s intervals (Fig. 3(c)). The averaged voltages were 1.38 V during 1-sun irradiation and 1.37 V during the self-discharge process. These voltages, which were detected after providing 1.0 mA current and before light irradiation, are higher than those observed under light irradiation of identical intensity with no pre-operation. Based on the calibration curve of the charging voltages over constant currents ranging from 0–1.0 mA, the detected value (1.38 V) can be theoretically reduced to the charging operation by applying a constant current of approximately 60 μ A. Notably, the self-discharge voltage is almost identical to the charging voltage under light irradiation, indicating the effectiveness of the photovoltaic charge.

The current densities of the TiO_2 on the FTO pre-coated glass substrate were measured at a bias of 0 V versus Ag/AgCl to verify their conductive properties using a three-electrode system in an electrolytic solution. The results indicate that the TiO_2 thin film is an insulator in the dark and acts as an *n*-type semiconductor under 1-sun light irradiation based on the anodic photocurrent density observed, as we reported previously.¹²

Thus, it can be assumed that the photovoltaic charging of the LIB requires the active materials on the anodic electrode to function as semiconductor to produce the electron-hole pair and as lithium ion conductors in their structures. Based on this assumption, there are numerous candidate active material for photovoltaic LIBs. Investigating both the physical and chemical properties of active materials used in anodic electrode is thus required to successfully obtain this type of innovative device.

The MPM is useful to obtain the active materials for the novel device which was functioned as the lithium ion battery, photovoltaic lithium ion battery, and the solar cell. This is the first report on translucent, thin-film LIB that can be charged by solar light irradiation was fabricated using active materials on a conductive glass substrate. The translucent, two-in-one device can simultaneously generate and store electricity from solar light and may be applied in smart windows, facilitating the use of renewable energy.

Acknowledgment

This work was supported by the Ministry of Education, Culture, Sports, Science, and Technology of Japan (MEXT) through its Supported Program for the Strategic Research Foundation at Private Universities, 2011–2015 (Kogakuin University–Energy Conversion Ecomaterials Center). This work was also supported by JSPS KAKENHI Grant Nos. 25410204 and 26810130.

References

1. H. Nagai et al., *Funct. Mater. Lett.* **6**, 1341001 (2013).
2. H. Zhang et al., *J. Phys. Chem. C* **111**, 6143 (2007).
3. P. F. Xiao et al., *Electrochim. Acta* **76**, 185 (2012).
4. Z. Yang et al., *J. Power Sources* **192**, 588 (2009).
5. G. S. Zakhrova et al., *J. Phys. Chem. C* **116**, 8714 (2012).
6. H. Nagai et al., *Sol. Energy Mater. Sol. Cells* **92**, 1136 (2008).
7. H. Nagai and M. Sato, *Heat Treatment: Conventional and Novel Applications* (InTech, Croatia, 2012).
8. H. Nagai et al., *Mater. Chem. Phys.* **137**, 252 (2012).
9. H. Nagai et al., *Sci. Adv. Mater.* **6**, 613 (2014).
10. Y. Li et al., *Appl. Phys. Lett.* **95**, 13102-1 (2009).
11. A. M. Stux et al., *J. Electrochem. Soc.* **152**, A2009 (2005).
12. L. S. Daniel et al., *J. Mater. Sci.* **48**, 7162 (2013).