

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

185,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Highly Functionalized Lithium-Ion Battery

Hiroki Nagai and Mitsunobu Sato

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/63491>

Abstract

Future energy demand is an important issue that requires consideration. Lithium-ion batteries (LIB) are one of the most popular types of rechargeable battery for portable electronic devices, such as mobile phones, cameras, and laptop computers, and have led to other applications being commercialized. Distributed power generation using renewable energy sources, such as solar photovoltaic (PV), can efficiently supply electricity according to on-site demand. If the electrodes of a LIB could function as a solar cell, the storage device could provide electricity without an electric power supply.

We have reported the fabrication of a thin-film LIB using the molecular precursor method. The thin-film LIB was fabricated with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for the anode and $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ for the cathode on a fluorine-doped tin oxide pre-coated glass substrate and an electrolyte of dissolved LiPF_6 . Moreover, we fabricated a novel LIB that was charged by light. This novel, translucent, thin-film LIB that can be charged by solar light irradiation was fabricated using active materials—titania for the anode and LiCoO_2 for the cathode—on a conductive glass substrate by a wet process.

This chapter focuses on the fabrication and properties of these multi-functional thin-film LIBs using a chemical method, viz., the molecular precursor method. The translucent device can simultaneously generate and store electricity from solar light and may be applied in smart windows, facilitating the wider use of renewable energy.

Keywords: lithium-ion battery, thin film, translucent, molecular precursor method, light irradiation

1. Introduction

Resource scarcity, energy, and global warming are all problems faced by modern society. In recent years, access to energy has become a particularly acute problem. Energy prices have

soared worldwide, and demand is increasing. One possible solution for these problems is the development of energy devices such as rechargeable batteries, solar cells, and fuel cells.

Lithium batteries using the Li metal or Li compounds as the anode have been studied over the past two decades; however, it has been the safety problems [1]. To overcome the problem, a safer approach has been to replace Li metal with a Li intercalation compound, usually a carbon compound, leading to the so-called “lithium ion” batteries (LIBs) [2–4]. The energy density of a LIB with high discharge voltage (3.6 V) is nearly twice that of Ni-Cd batteries, and excellent cycle life and a higher level of intrinsic safety have been demonstrated. Currently, the rechargeable LIB is one of the most popular types of rechargeable battery for portable electronic devices such as mobile phones, cameras, and laptop computers. Many other LIB applications have also been commercialized. In particular, micro-sized LIBs have attracted much interest for use as power sources for smart cards, implantable medical devices, and micro-sensors.

We recently fabricated a transparent thin-film LIB using the molecular precursor method (MPM) [5]. The device was fabricated with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) as the anode and $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ (LFP) as the cathode on a fluorine-doped tin oxide (FTO) pre-coated glass substrate, with an electrolytic solution of LiPF_6 . We discovered that this novel LIB is also electrochromic, that is, it colors and discolors according to charge and discharge operations, respectively. This type of electrochromic device can be used in various monitoring systems, electrically controllable tint glass, and so on. If the electrodes of a LIB could also function as a solar cell, the storage device could then provide electricity without an electric power supply.

2. Principle of the molecular precursor method

The MPM is one of the wet processes used for thin film fabrication of various metal oxides, including metal oxides or calcium phosphate compounds [6]. This method is based on the design of metal complexes in coating solutions with excellent stability, homogeneity, miscibility, and coatability, and so on. These highly stable metal-complex anions are highly soluble in water and can thus be dissolved in volatile solvents by combining them with appropriate alkylamines. Furthermore, the resultant solutions can generally form excellent precursor films using various coating procedures such as spin coating. The precursor films produced from metal complexes should be amorphous, similar to films produced by metal/organic polymers in sol-gel processes; otherwise, it would not be possible to fabricate homogeneous metal-oxide thin films on substrates using heat treatment methods.

A stable metal complex is dissolved at a molecular level in the precursor solution. The metal complex salt in the precursor film must be amorphous before heat treatment to fabricate thin films without cracks and pinholes. The alkylamines play an important role in obtaining an amorphous salt in the precursor film. The plausible packing of the metal complex in the precursor film formed on the substrate can be theoretically explained using molecular dynamics. The shrinkage rate of the film in the vertical direction can be estimated from the model structure before heat-treatment based on the crystal structure of the metal complex salt, which can be obtained as a single crystal when the alkyl groups in the amines are short enough.

The shrinkage rate in the sol-gel method is usually considered to be around 10 times. However, it is roughly estimated to be 10–15 times in the case of MPM, on the basis of the crystal structures (**Figure 1**). Thus, the densification degrees of the precursor films during heat treatment in the process of MPM are similar to those from sol-gel procedures, even though the precursor films involve alkylamines and ligands.

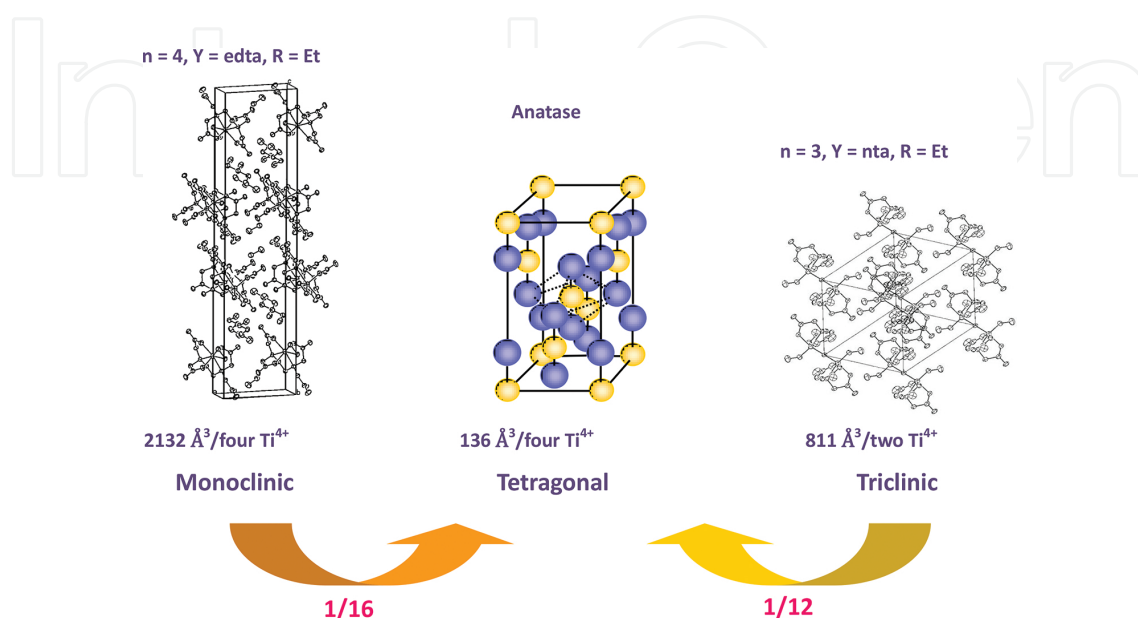


Figure 1. Schematic for shrinkage models of metal complex film (left side: Ti-edta complex; right side: Ti-nta complex).

3. Electrochromism of the transparent LIB

Recently, 3-D structures formed from compounds such as PO_4 tetrahedra and FeO_6 octahedra have created interest for their potential use as cheap positive electrodes for lithium-ion batteries. Efforts toward this relatively novel class of intercalation hosts for lithium have focused on systems such as the olivine $\text{Li}_{1-x}\text{FePO}_4$ and NASICON compositions $\text{Li}_x\text{Fe}_2(\text{SO}_4)_3$ or $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ (LFP) into which reduction/oxidation of $\text{Fe}^{3+}/\text{Fe}^{2+}$ occurs at potentials close to 3.43, 3.55, and 2.8 V vs. Li/Li^+ , respectively [7–10].

Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) is a promising anode material for LIBs. This material exhibits very flat discharge and charge curves and only a small structural change during charge-discharge processes. The theoretical specific capacity of this material is 175 mA h g^{-1} and exhibits a practical specific capacity as high as $150\text{--}160 \text{ mA h g}^{-1}$ after 100 discharge cycles. During this process of Li^+ intercalation and de-intercalation, the cubic symmetry of the parent spinel is Unaffected by lithiation; the lattice parameter (8.36 Å) and unit-cell volume are virtually unaltered by the phase transition. The lack of significant changes to the crystallographic parameters is remarkable and provides a structure that is extremely tolerant to electrochemical cycling. At the same time, the improved safety and reliability of the spinel compared with that

of carbon electrodes make the LIBs using LTO as anode material suitable for electric vehicle (EV) and power storage batteries [11–15].

We attempted to fabricate a transparent thin-film LIB using the MPM. A transparent LFP thin-film cathode of 80 nm thickness was fabricated on a conductive FTO pre-coated glass substrate by heat treating a precursor ethanolic solution containing a Li(I) complex of nitrilotriacetic acid (NTA), an Fe(III) complex of ethylenediaminetetraacetic acid (EDTA), and (dibutylammonium)₂H₂P₂O₇·0.5H₂O at 550 °C for 10 min in air. A transparent LTO thin-film anode of 90 nm thickness was also fabricated on the substrate by heat treating a precursor ethanolic solution containing a Li(I) complex of NTA, a Ti(IV) complex of NTA, and hydrogen peroxide, at 550 °C for 30 min in air. The rechargeability of the assembled sandwich-type battery using an electrolytic solution dissolving LiPF₆ was measured by a repeated charge and discharge test.

The weight loss of 17% accompanied by an endothermic peak in the temperature range from 100 to 200 °C appeared in the TG-DTA curves of the LTO precursor gel (**Figure 2**). The TG curve shows that the compound decomposed by 600 °C with a final residual weight of 13%. The Li₄Ti₅O₁₂ powders are usually synthesized by a solid-state reaction of lithium and titanium salts [16, 17]. However, there are some disadvantages to solid-state reactions, such as inhomogeneous distribution, lack of stoichiometric control, and so on [18]. Hao and co-workers fabricated a spinel-type Li₄Ti₅O₁₂ by a modified sol-gel method using oxalic acid as a chelating agent. According to the TG-DTA results of the report, the final weight loss from 700 to 800 °C is mainly attributed to the thermal decomposition of residual carbonate phases and the completion of the crystallization to Li₄Ti₅O₁₂. These results correspond to the following reaction:

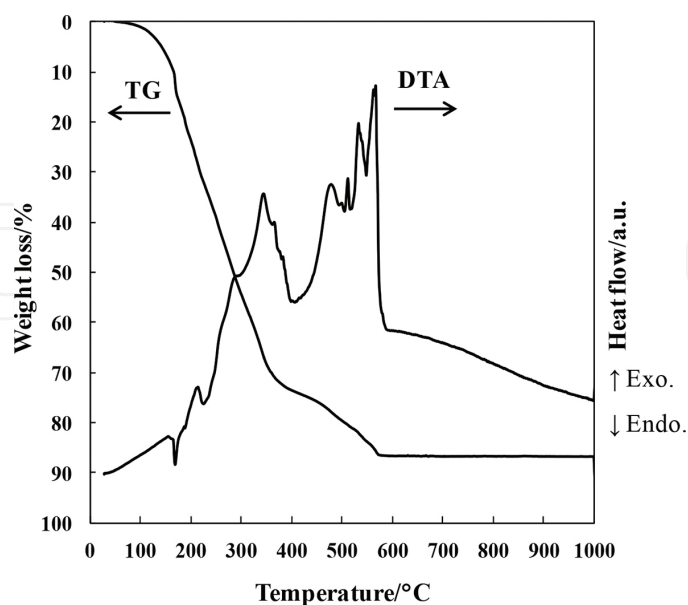
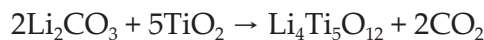


Figure 2. The TG-DTA curves of the LTO precursor gel obtained by evaporating the precursor solution. The measurement temperature was increased from 25 to 1000 °C at a rate of 10 °C min⁻¹ using an air flow rate of 0.1 L min⁻¹.

However, in the case of MPM, no reaction occurs between 700 and 800°C from the TG-DTA results. Thus, it is significantly suggested that the chelating ligand in the molecular precursors successfully prevents any unexpected segregation of the metal compounds during oxide formation because the discrete molecular precursor complexes provide homogeneous and ideal mixtures of the different metal species at the molecular level in the precursor films.

The repeated charge and self-discharge tests of the assembled LIB were successfully performed at a constant current of 10 μA , and the curve of the voltage change is shown in **Figure 3**. A maximum voltage of 3.6 V was recorded when the current was applied at intervals of 20 sec.

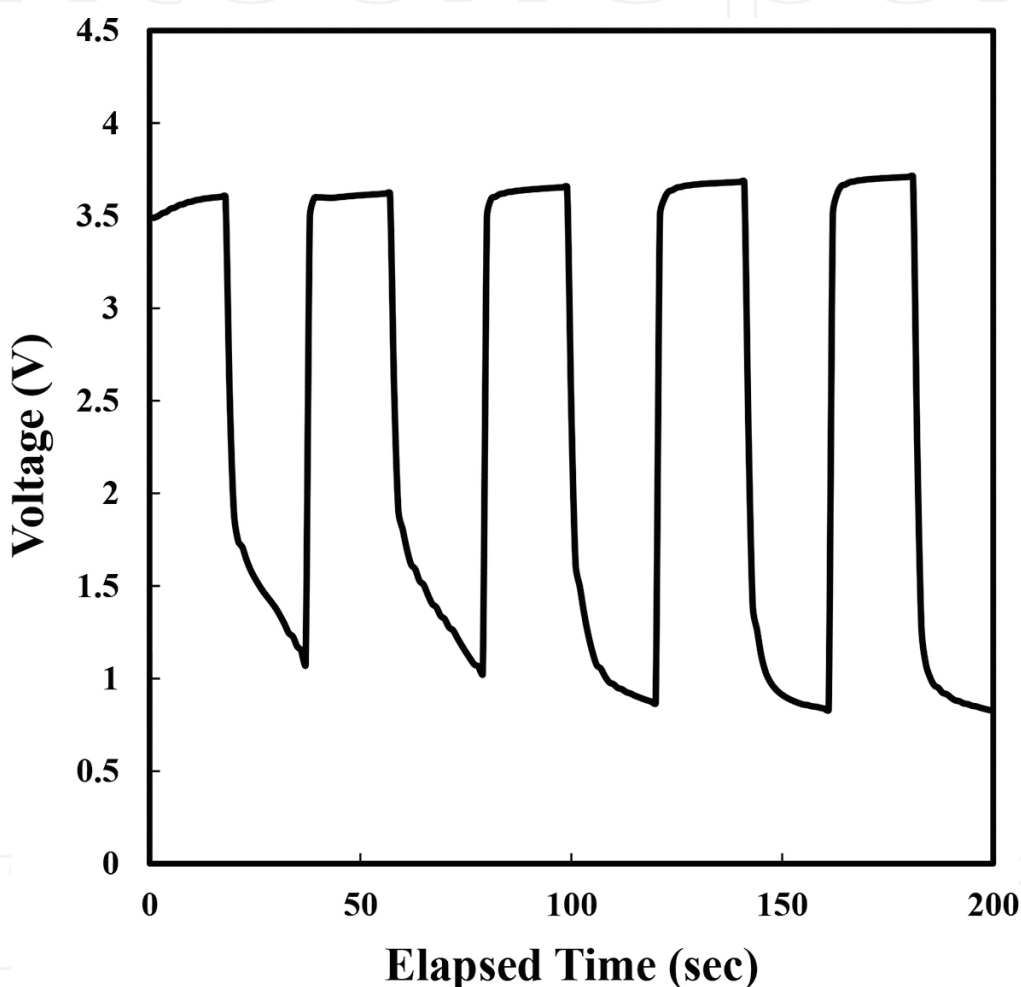


Figure 3. The repeated charge and discharge test of the battery. The charge at the constant current of 10 μA and spontaneous discharge was repeated at 20-s intervals.

When the battery was charged from an external source, the colorless battery drastically changed color to blue-gray, as shown in **Figure 4**. The color changes were repeatable and occurred simultaneously with the charge and discharge operations. The transmittance spectra of the charged and discharged battery are shown in **Figure 5**, and it is apparent that the colored battery after charging recovers repeatedly to a colorless one after spontaneous discharge. The specific coloration of the LTO electrode was confirmed by disassembling the colored battery.

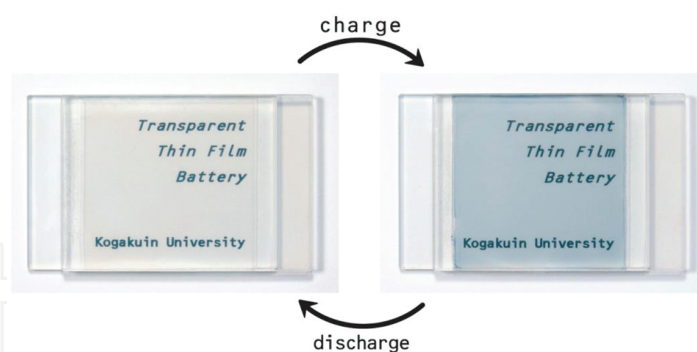


Figure 4. The colorless battery before charge and after discharge (left) and blue-gray battery after charge (right).

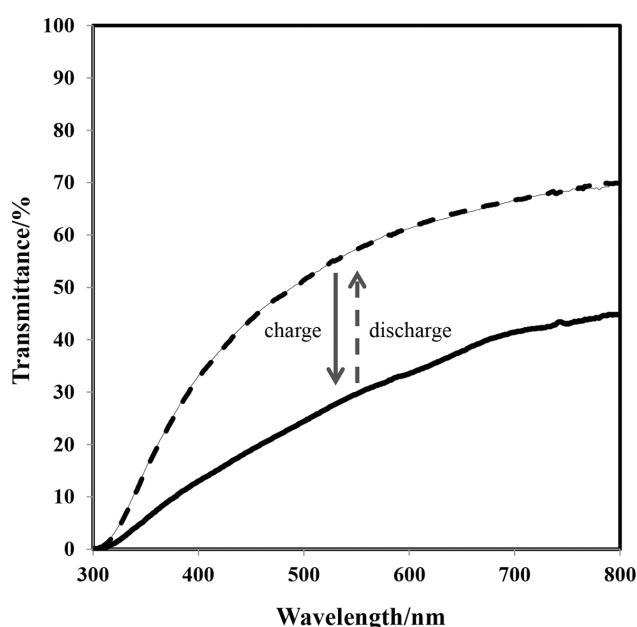
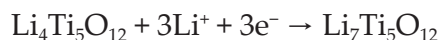


Figure 5. UV-vis spectra of the before/after charge and after discharge of the battery. The lines indicate the following: —, before charge; ---, after charge; - · -, after discharge.

This unprecedented phenomenon suggests a two-step reaction based on the $\text{Ti}^{4+}/\text{Ti}^{3+}$ redox coupling with the intercalation of Li^+ ions into the spinel-type LTO electrode. The electrochemical reaction can be described as follows [19]:



The intercalation of Li^+ ions occurred in the vacant sites of the LTO spinel-skeleton through the electrolytic solution, and an equivalent amount of Li^+ ions were supplied from the LFP electrode by the charge operation. The coloration of the LTO to blue-gray in the process suggests that some of the Ti^{4+} sites were simultaneously reduced to Ti^{3+} ions by the electrons supplied from the power source. The Ti^{3+} ions could again be oxidized to Ti^{4+} ions along with the self-discharge of the battery, when the intercalated Li^+ ions returned to the LFP electrode through the electrolytic solution. Thus, the reversible LIB reaction could be visualized using

the thin-film electrodes fabricated by this method. This monitoring system might be useful for clarifying the reaction mechanism of the novel LIB.

The rechargeable properties of this present LIB assembled with the newly fabricated ceramic thin films were examined by repeated charge and discharge testing. It is remarkable that the electrochromic reactions synchronous to the charge and discharge operations of the transparent thin-film battery can be clearly observed. Thus, the transparent thin-film device fabricated by the MPM may be applied to monitoring the redox reaction in electrochemical devices such as LIBs. The suitability of the MPM, as shown in this work, may also be useful for the production of transparent thin films of metal oxides and phosphates on large-surface-area materials.

4. Photovoltaic LIB

Titania has been used as a white pigment for paints, cosmetics, and foodstuffs [20]. When titania particles absorb UV radiation, they produce pairs of electrons and holes inside the particles. The surface states of the titania particle are important for photoreactivity because the photo-induced electrons and holes can be incorporated into redox reactions on the titania surface before spontaneous recombination [21–37].

Zhang et al. [38] reported that anatase 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. In fact, titania has negligible toxicity, excellent cyclability, and chemical stability in LIBs [39, 40]. Additionally, anatase nanotubes have also been characterized as active materials and have been shown to have electrochemical potentials of 1.5–1.7 V vs. Li/Li⁺ [41]. 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 thin-film titania and the abovementioned LIB using the MPM. We attempted to fabricate a novel thin-film LIB that could be charged by light irradiation based on these results [42]. This novel, translucent, solar-chargeable LIB was fabricated using titania (anode) and LiCoO₂ (cathode) thin films prepared by MPM as the active materials on the above-mentioned conductive glass substrate. The precursor solutions containing the corresponding complexes capable of producing the anode and cathode active materials were easily prepared. Precursor films of TiO₂ and LiCoO₂ on the FTO pre-coated glass substrate were separately formed via a spin-coating method at ambient temperature using a two-step process, and they were pre-heated in a drying oven at 70 °C for 10 min. Then, the precursor films were heat treated in air for 30 min at 500 and 550 °C, respectively.

The X-ray diffraction peaks of the resulting thin films can be attributed to anatase and LiCoO₂. The optical transmittance of the assembled device was 50% at 700 nm, which is the longest wavelength in the visible region; hence, the device is translucent. A typical charge/discharge cyclic test was performed with a DC voltage source/monitor and was repeated 10 times at 20-sec intervals. The averaged potential at 2.34 V was observed by applying a constant

current of 1.0 mA, then that at 2.01 V was detected after 20 sec during the sequential self-discharge process (**Figure 6**).

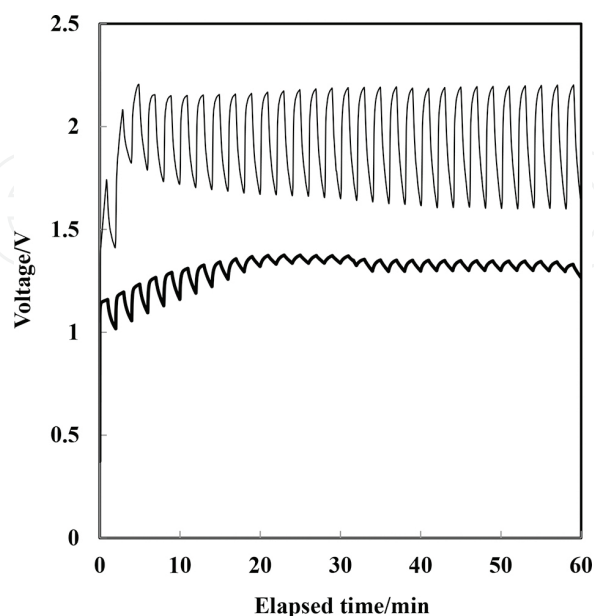
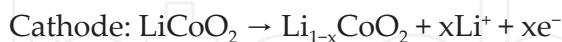


Figure 6. The charge/discharge cyclic test of the assembled battery. The lines indicate the following: ———, a constant current of 0.2 mA; - - - - - , 1-sun irradiation.

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 follows:



The repeated charge and self-discharge test of the LIBs performed in this study was also conducted under light irradiation and in the dark with no electrical supply 30 times at 60-sec 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 also shown in **Figure 6**. The averaged voltages were 1.32 V during 1-sun irradiation and 1.29 V in the dark during the self-discharge process. Based on the calibration curve of the charging voltages over constant currents ranging from 0 to 1.0 mA, the detected value (1.38 V) can be theoretically reduced to the charging operation by applying a constant current of approximately $60 \mu\text{A}$ (**Figure 7**). Notably, the self-discharge voltage is almost identical to the charging voltage under light irradiation, indicating the effectiveness of the photovoltaic charge. The J-V curve of this LIB was measured under simulated sunlight AM 1.5 from a solar simulator with the radiant power of 1 -sun (**Figure 8**). It was found that the LIB generated

photocurrent with short-circuit current; $I_{sc} = 7 \times 10^{-5}$ A, open-circuit voltage; $V_{oc} = 0.97$, fill factor; $ff = 0.29$ and a photo conversion efficiency of 0.02%. Thus, this LIB can also work as a solar cell.

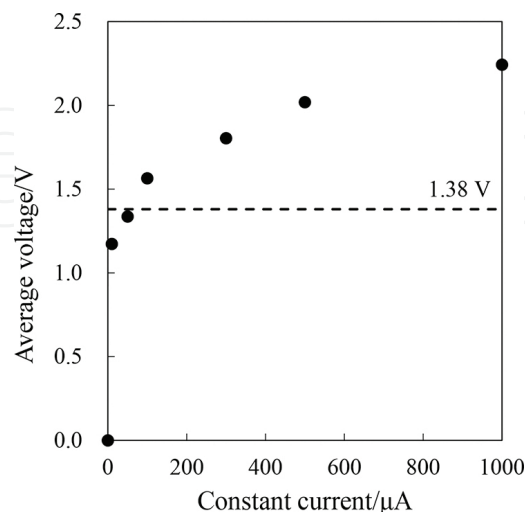


Figure 7. The averaged charging voltages over constant currents ranging from 0 to 1.0 mA.

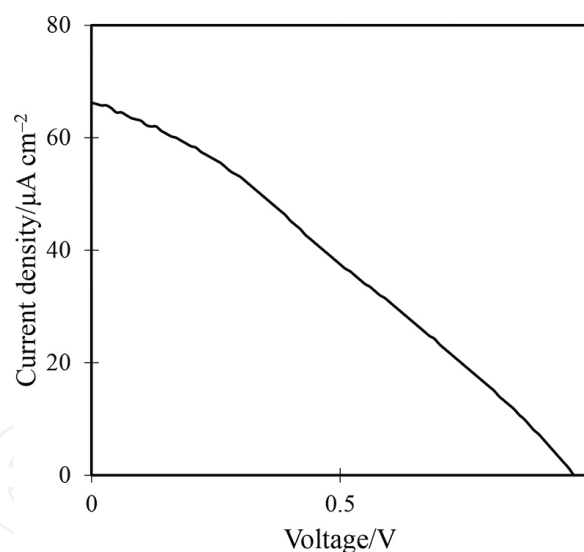


Figure 8. The photocurrent density-voltage characteristics (J-V curves) of LIB.

The current densities of the TiO_2 and LiCoO_2 on the FTO pre-coated glass substrate were measured at a bias of 0 V vs. 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 (**Figure 9**), as we reported previously [43]. It can be assumed that the photovoltaic charging of the LIB requires the active materials on the anodic electrode to function as a semiconductor to produce electron-hole pairs and as lithium-ion

conductors in their structures. Based on this assumption, there are numerous candidate active materials for photovoltaic LIBs. Investigating both the physical and chemical properties of active materials used in electrodes is thus required to successfully fabricate this type of innovative device.

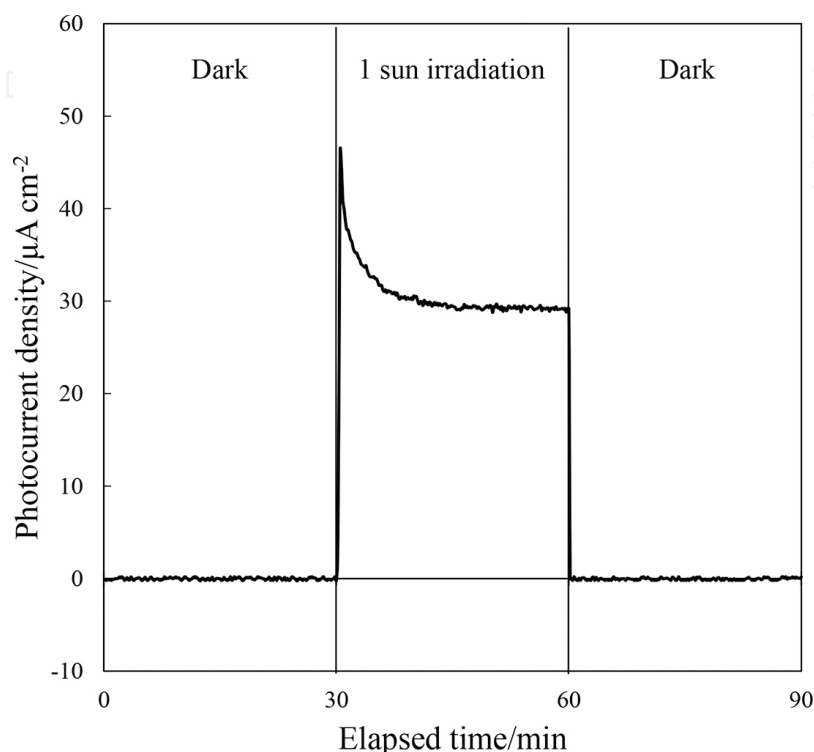


Figure 9. Photocurrent densities of anatase thin film fabricated on FTO glass. The photocurrent density of the sample electrode was measured under 1 sun light irradiation.

These results indicate that the translucent, two-in-one device can simultaneously generate and store electricity by irradiation with solar light and may be applicable for use as a multi-functional window, and facilitating the wider use of renewable energy.

5. Conclusion

The molecular precursor method is useful to obtain the active materials for the novel device which functioned as the lithium-ion battery, photovoltaic lithium-ion battery, and the solar cell. This is the original 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 molecular precursor method was developed in our studies just 20 years ago. At that time, we reported the fabrication of Co_3O_4 and TiO_2 thin films. We subsequently reported the fabrication of thin films of various materials such as Cu_2O , SiO_2 , ZnO , and apatite. This method is pertinent to coordination chemistry, materials science, nanoscience, and nanotechnology, and it has provided various thin films of high quality.

Author details

Hiroki Nagai and Mitsunobu Sato*

*Address all correspondence to: ft10302@ns.kogakuin.ac.jp

Department of Applied Physics, School of Advanced Engineering, Kogakuin University,
Tokyo, Japan

References

- [1] Wakihara M., Yamamoto O. Lithium ion batteries fundamentals and performance. Weinheim: WILEY-VCH Verlag GmbH; 1998.
- [2] Murphy D. W., Carides J. N. Low voltage behaviour of lithium/metal dichalcogenide topochemical cells. *J. Electrochem. Soc.* 1979;126:349–351.
- [3] Lazzari M., Scrosati B. A cyclable lithium organic electrolyte cell based on two intercalation electrodes. *J. Electrochem. Soc.* 1980;127:773–774.
- [4] Nagaura T, Tazawa K. Lithium ion rechargeable battery. *Prog. Batt. Solar Cells.* 1990;9:20–29.
- [5] Nagai H., et al. Synchronous electrochromism of lithium ion battery with chemically fabricated transparent thin films. *Funct. Mater. Lett.* 2013;6:1341001–1341008.
- [6] Nagai H., Sato M. Heat treatment in molecular precursor method for fabricating metal oxide thin films. In: Frank C ed. *Heat Treatment—Conventional and Novel Applications*. Rijeka: InTech; 2012. pp. 103–128.
- [7] Patoux S., Wurm C., Morcrette M., Rousse G., Masquelier C. A comparative structural and electrochemical study of monoclinic $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. *J. Power Sources.* 2003;119:278–284.
- [8] Yin S. C., Grondy H., Strobel P., Huang H., Nazar L. F. Charge ordering in lithium vanadium phosphates: electrode materials for lithium-ion batteries. *J. Am. Chem. Soc.* 2003;115:326–327.
- [9] Masquelier C., Padhi A. K., Nanjundaswamy K. S., Goodenough J. B. New cathode materials for rechargeable lithium batteries: the 3-D framework structures $\text{Li}_3\text{Fe}_2(\text{XO}_4)_3$ ($\text{X}=\text{P}, \text{As}$). *J. Solid. State. Chem.* 1998;135:228–234.
- [10] Morgan D., Ceder G., Saidi M. Y., Barker J., Swoyer J., Huang H., Adamson G. Experimental and computational study of the structure and electrochemical properties of $\text{Li}_x\text{M}_2(\text{PO}_4)_3$ compounds with the monoclinic and rhombohedral structure. *Chem. Mater.* 2002;14:4684–4693.

- [11] Colbow K. M., Dahn J. R., Haering R. R. Structure and electrochemistry of the spinel oxides LiTi_2O_4 and $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$. *J. Power Sources*. 1989;26:397–402.
- [12] Nishizawa M. Measurements of chemical diffusion coefficient of lithium ion in graphitized mesocarbon microbeads using a microelectrode, *electrochemi. Solid State Lett.* 1998;1:10–12.
- [13] Ohzuku T., Iwakoshi Y., Sawai K. Formation of lithium-graphite intercalation compounds in nonaqueous electrolytes and their application as a negative electrode for a lithium ion (Shuttlecock) cell. *J. Electrochem. Soc.* 1993;140:2490–2497.
- [14] Zaghib K., Armand M., Gauthier M. Electrochemistry of anodes in solid-state Li-ion polymer batteries. *J. Electrochem. Soc.* 1998;145:3135–3140.
- [15] Ferg E. Spinel Anodes for lithium-ion batteries. *J. Electrochem. Soc.* 1994;141:147–150.
- [16] Ohzuku T., Ueda A, Yamamoto A. Zero-strain insertion material of $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ for rechargeable lithium cells. *J. Electrochem. Soc.* 1995;142:1431–1435.
- [17] Kanamura K, Umegaki T., Naito H., Takehara Z., Yao T. et al., Structural and electrochemical characteristics of $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ as an anode material for rechargeable lithium batteries. *J. Appl. Electrochem.* 2001;31:73–78.
- [18] Y. J. Hao et. al., Synthesis and characterization of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode material by oxalic acid-assisted sol–gel method. *J. Power Sources* 2006;158:1358–1364.
- [19] Mosqueda H. A., Vazquez C., Bosch P., Pfeiffer H. Chemical sorption of carbon dioxide on lithium oxide. *Chem. Mater.* 2006;18:2307–2310.
- [20] Hashimoto K., Irie H., Fujishima A. TiO_2 photocatalysis: A historical overview and future prospects. *AAAPS. Buliten.* 2007;17:12–28.
- [21] Fujishima A., Honda K. Electrochemical photolysis of water at a semiconductor electrode. *Nature.* 1972;238:37–38.
- [22] Serpone N., Pelizzetti E. Fundamental studies into primary events in photocatalysis employing CdS and TiO_2 semiconductors: Photoluminescence, laser flash photolysis and pulse radiolysis. In: *Homogeneous and Heterogeneous Photocatalysis*. D. Reidel Publishing Company. Dordrecht; 1986. pp. 51–90.
- [23] Serpone N., Pelizzetti E. *Photocatalysis, Fundamentals and Applications*. New York: John Wiley & Sons; 1989.
- [24] Kamat P. V. Photochemistry on nonreactive and reactive (semi-conductor) surfaces. *Chem. Rev.* 1993;93:267–300.
- [25] Ollis D. F. Photocatalytic purification and treatment of water and air. Al-Ekabi H ed. Amsterdam: Elsevier; 1993. 820 p.
- [26] Heller A. Chemistry and applications of photocatalytic oxidation of thin organic films. *Acc. Chem. Res.* 1995;28:503–508.

- [27] Hoffmann M. R., Martin S. T., Choi W., Bahnemann D. W. Environmental applications of semiconductor photocatalysis. *Chem. Rev.* 1995;95:69–96.
- [28] Mills A., Lechante S. An overview of semiconductor photocatalysis. *J. Photochem. Photobiol. A: Chem.* 1997;108:1–35.
- [29] Peral J., Domènech X., Ollis D. F. Heterogeneous photocatalysis for purification, decontamination and deodorization of air. *J. Chem. Tech. Biotech.* 1997;70:117–140.
- [30] Fujishima A., Hashimoto K., Watanabe T. *TiO₂ photocatalysis: fundamentals and applications*. Tokyo: BKC, Inc; 1999. 184 p.
- [31] Fujishima A., Rao T. N., Tryk D. A. Titanium dioxide photocatalysis. *J. Photochem. Photobiol. C.* 2000;1:1–21.
- [32] Ollis D. F. Photocatalytic purification and remediation of contaminated air and water. *C. R. Acad. Sci. Paris, Serie II C, Chim.* 2000;3:405–411.
- [33] Tryk D. A., Fujishima A., Honda K. Recent topics in photoelectrochemistry: achievements and future prospects. *Electrochim. Acta.* 2000;45:2363–2376.
- [34] Fujishima A., Tryk D. A., Bard A. J., Stratmann M. Fundamentals of Photocatalysis. In: Licht S, ed. *Encyclopedia of Electrochemistry*. Vol. 6: Semiconductor Electrodes and Photoelectrochemistry. Weinheim; Wiley-VCH; 2002. 608 p.
- [35] Hashimoto K., Irie H., Fujishima A. *TiO₂ photocatalysis: a historical overview and future prospects*. *Japan. J. Appl. Phys.* 2005;44:8269–8285.
- [36] Fujishima A., Zhang X. Titanium dioxide photocatalysis: present situation and future approaches. *C. R. Chimie.* 2006;9:750–760.
- [37] Fujishima A., Zhang X., Tryk D. A. Heterogeneous photocatalysis: from water photolysis to applications in environmental cleanup. *Internat. J. Hydrogen Energy.* 2007;32:2664–2672.
- [38] Zhang H., et al. Electrochemical lithium storage of titanate and titania nanotubes and nanorods. *J. Phys. Chem. C.* 2007;111:6143–6148.
- [39] Ortiz G. F., et al. Alternative Li-ion battery electrode based on self-organized titania nanotubes. *Chem. Mater.* 2009;21:63–67.
- [40] Yang Z., et al. Nanostructures and lithium electrochemical reactivity of lithium titanates and titanium oxides: a review. *J. Power Sources.* 2009;192:588–598.
- [41] Zakharova G. S., et al. Anatase nanotubes as an electrode material for lithium-ion batteries. *J. Phys. Chem. C.* 2012;116:8714–8720.
- [42] Nagai H., Suzuki T., Takahashi Y., Sato M. Photovoltaic lithium ion battery fabricated by molecular precursor method. *Funct. Mater. Lett.* in print.

- [43] Daniel L. S., Nagai H., Sato M. Absorption spectra and photocurrent densities of Ag nanoparticle/TiO₂ composite thin films with various amounts of Ag. J. Mater. Sci. 2013;48:7162–7170.

IntechOpen

IntechOpen