Light energy storage in TiO_2/MnO_2 composite electrode for photoelectrochemical capacitor

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Abstract

Composite electrodes comprising TiO_2 and MnO_2 particles were prepared as photoelectrochemical capacitor electrodes that enable both photoelectric conversion and energy storage. A MnO_2 electrode was also prepared for characterization of MnO_2 alone, and its electrochemical capacitor property was evaluated. The MnO_2 electrode showed higher specific capacitance than a RuO_2 electrode. Results of the photoelectrochemical measurements demonstrated that the discharge capacity of the TiO_2/MnO_2 composite electrode was slightly inferior to that of the TiO_2 and RuO_2 electrodes using. By reducing MnO_2 particle size, the composite electrode exhibited increased surface roughness and enhanced capacity. We consider that the smaller MnO_2 particles can efficiently store Na^+ ions even at a low photo-charge voltage of TiO_2.

Keywords: Photoelectrochemical capacitor; Composite electrode; Rutile-type titanium oxide; Manganese oxide

1. Introduction

In realizing a low-carbon society, promotion of renewable energy, particularly solar energy, will play a crucial role. However, a disadvantage of solar energy is that solar irradiance strongly varies depending on weather, time of day, and location, resulting in unstable power generation and a demand for energy storage. Electricity generated by a photovoltaic cell is generally stored using a Li-ion battery or an electrochemical capacitor connected to the cell via an external circuit. Another disadvantage is the low power density (1.36 kW m^{-2}) of solar irradiance. Thus, solar power is unfavorable for current portable electronic devices with high power demands; however, it will be sufficiently useful for next-generation display devices like electronic paper, which have much lower power consumption. To increase storage efficiency and decrease device size, a single electrode should achieve both photoelectric conversion and energy storage, as some researchers have reported [1-3].

Titanium dioxide (TiO_2) is a popular photo-semiconductor with excellent chemical stability in aqueous solution. Photoexcited electrons are generated by irradiation of the TiO_2 electrode, which reduce other transition metal oxides; thus TiO_2 electrodes can act as energy-storage electrodes. Joudkazytė *et al.* have recently developed a photoelectrochemical capacitor consisting of two electrodes: a TiO_2 electrode for power generation and a RuO_2 electrode for energy storage in aqueous solution [4]. Tatsuma *et al.* have reported a photoelectrochemical capacitor comprising a TiO_2 electrode and a WO_3 electrode [5], used for power generation and energy storage, respectively. The material costs of RuO_2 and WO_3 are higher than the cost of TiO_2. In this study, we chose MnO_2 as the energy storage material because of its lower cost, and a novel single electrode comprising a TiO_2/MnO_2 composite was prepared as a photoelectrochemical capacitor.

2. Materials and Methods

2.1. Active materials of electrodes

As-received manganese dioxide powder (ε-MnO_2, Akhtenskite, Wako Pure Chemical Industries) was used as the active material. The MnO_2 powder has an average particle size of

11.8 μm and crystallite size of 11.6 nm (Fig. S1 and Fig. S2 in Supporting Information). To reduce the particle size of MnO_2, a mechanical milling treatment was conducted by a high-energy planetary ball mill (P-6, Fritsch) for 1 h with a rotational speed of 380 rpm. For the photo-semiconductor, we used titanium dioxide powder (rutile TiO_2, Wako Pure Chemical Industries) with a particle size of 213 nm and crystallite size of 41.1 nm. Thick-film electrodes of TiO_2/MnO_2 composite were prepared by the gas-deposition (GD) method [6,7]. The detailed procedures are described in Fig. S3.

2.2. Charge–discharge tests as electrochemical capacitor

Conventional charge–discharge tests were conducted in a beaker-type three-electrode cell (HX-113, Hokuto Denko Co., Ltd.). A titanium wire and a Ag/AgCl electrode were used as the counter and reference electrodes, respectively. The electrolyte was a Na_2SO_4 aqueous solution with a concentration of 0.5 mol L^{-1}. Galvanostatic charge–discharge method was applied using a battery test system (HJ-1001 SM8A, Hokuto Denko Co., Ltd.) with a potential range of 0.04–0.84 V under 200 mA g^{-1} at 303 K. By a linear approximation for the charge–discharge curves, the specific capacitance C_s was calculated using the capacitance calculator software (SD8 CAR, Hokuto Denko Co., Ltd.) and the following equation:

$$C_s = I / [(dV/dt)\, m)]$$

where I is the charge–discharge current, dV/dt is the scan rate, and m is the active material mass.

2.3. Photoelectrochemical measurements

Photoelectrochemical measurements were performed using the same cell as the electrochemical capacitor test. Our newly developed measurement system is shown in Fig. 1. As a solar simulator, a Xe lamp (SOLAX XC-100EFSS, SERIC Co., Ltd.) with a power density of about 1.0 kW m^{-2} was used. In a photo-charge process, the TiO_2/MnO_2 electrode was irradiated for 10 s in open-circuit condition. A discharge process was subsequently performed for 20 s in short-circuit condition between the TiO_2/MnO_2 electrode and the Ti electrode. For a control experiment, the discharge current was measured after the electrodes were kept in open-circuit condition for 10 s without irradiation (a dark-charge process). Typical variations in potential and current density are shown in Fig. S5. The discharge capacity was defined as an integrated

difference between the two kinds of discharge currents after the photo-charge dark-charge processes during the first cycles (Fig. S6).

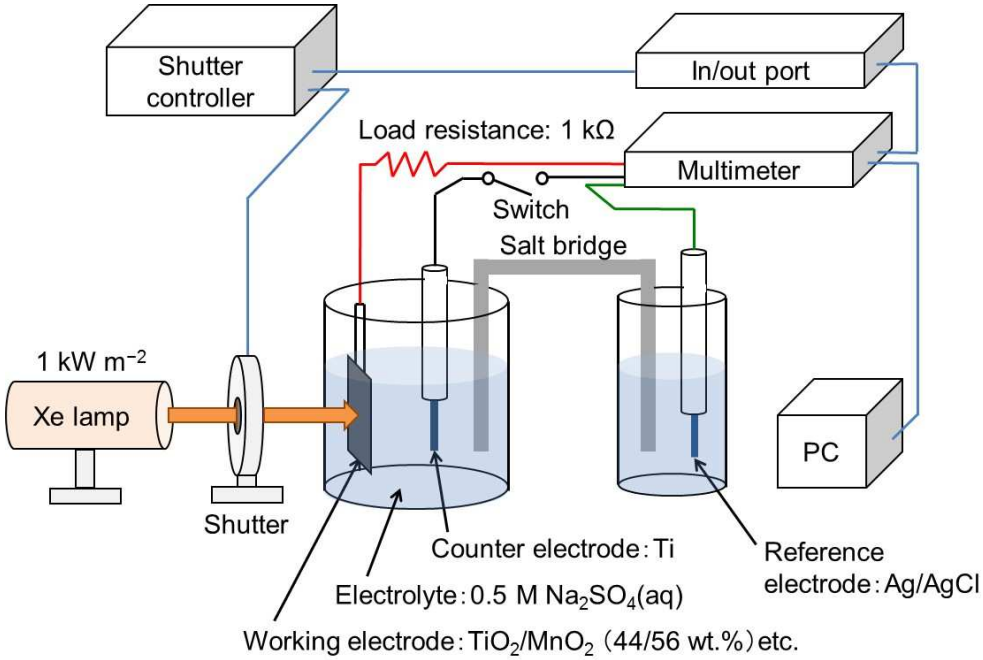

Figure 1. Schematic illustration of measurement system for photoelectrochemical capacitor electrode.

3. RESULTS AND DISCUSSION

3.1. Electrochemical properties as capacitor electrode.

The charge–discharge curve of the RuO_2 electrode shows a symmetric profile (Fig. S4(a)), indicating typical pseudo-capacitive characteristics and a reversible redox-based variation of oxidation states among Ru^{4+}, Ru^{3+}, and Ru^{2+}. On the other hand, the MnO_2 electrode exhibits a large potential drop at the beginning of the discharge process (Fig. S4(b)), probably due to the large overpotential caused by the much lower electronic conductivity of MnO_2 (10^{-6} S cm^{-1}) than RuO_2 (10^4 S cm^{-1}), which indicates that the electrode reaction is limited to the surface of the MnO_2 electrode. The pseudo-capacitance of MnO_2 arises from the Mn^{4+}/Mn^{3+} redox reaction at the surface of MnO_2 particles [8]. ε -MnO_2 has one-dimensional tunnel structures of 1×1 and

1×2, corresponding to sizes of 0.23 nm × 0.23 nm and 0.23 nm × 0.46 nm, respectively [9]. To retain charge balance of reduced MnO_2, Na^+ ions of the electrolyte are inserted into the tunnel structures on the MnO_2 surface because the ionic diameter of a Na^+ ion (0.204 nm) is smaller than either tunnel size.

Figure 2 shows the specific capacitance variation for the MnO_2 electrode versus cycle number. The capacitances for the RuO_2 and TiO_2 electrodes were plotted for comparison. The capacitance of the TiO_2 electrode was almost 0 F g^{-1}, suggesting that no electrochemical redox reaction occurs in the potential range of 0.0–0.8 V vs. Ag/AgCl. We have previously reported that Na-insertion into rutile TiO_2 can occur in the potential range of 0.1–0.7 V vs. Na^+/Na [10], which corresponds to the potential range of −2.4 to −1.8 V vs. Ag/AgCl. The RuO_2 electrode maintained a constant capacitance of 320–330 F g^{-1}, which is smaller than the typical capacitances of 500–600 F g^{-1} [11]. This is attributed to the preparation method in this study: the electrodes do not include any binder or conductive additive for the fundamental evaluation. The MnO_2 electrode exhibited a larger capacitance of 276 F g^{-1} in the first cycle, although rapid capacitance decay was observed for the initial ten cycles. The capacitance decay presumably arises from an irreversible change in the MnO_2 crystal structure.

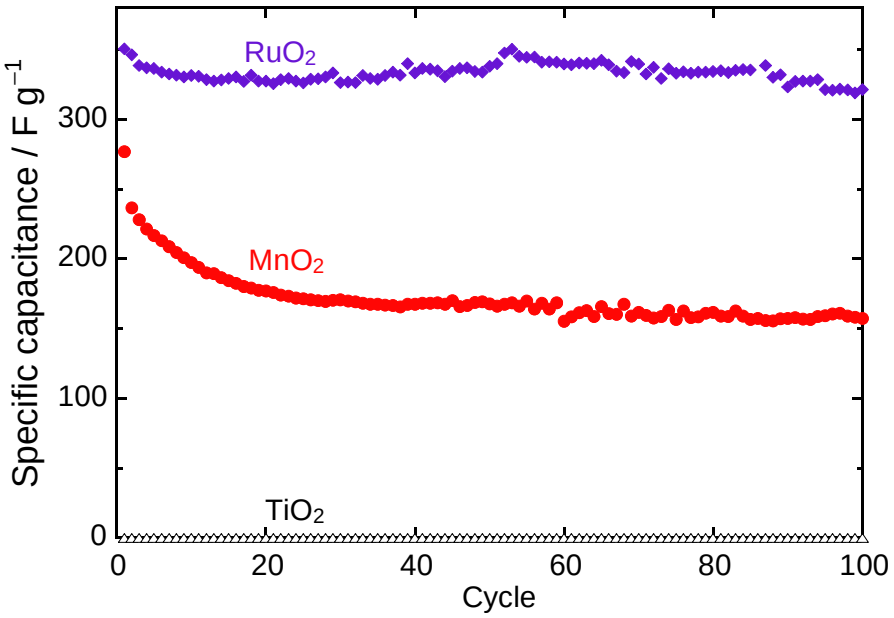

Figure 2. Dependence of specific capacitance on cycle number for MnO_2 electrode as electrochemical capacitor. For comparison, we prepared RuO_2 electrode and TiO_2 electrode, and evaluated their specific capacitances.

3.2. Charge–discharge properties as photoelectrochemical capacitor.

Figure 3(a) represents the discharge capacity of the composite electrode prepared using TiO_2 and as-received MnO_2. In this study, a TiO_2/RuO_2 composite electrode was also prepared and evaluated for comparison. The discharge capacity of this composite electrode (Fig. S7) was inferior to that obtained by other researchers for a photoelectrochemical capacitor comprised of individual TiO_2 and RuO_2 electrodes [4]. Thus, Fig. S7 shows the value of their work as a standard. The TiO_2 electrode delivered a capacity of only 8.7 mA h g^{-1}. Compared to this, the TiO_2/MnO_2 composite electrode presented a higher capacity of 30 mA h g^{-1}. However, this capacity is slightly inferior to the TiO_2/RuO_2 composite electrode [4].

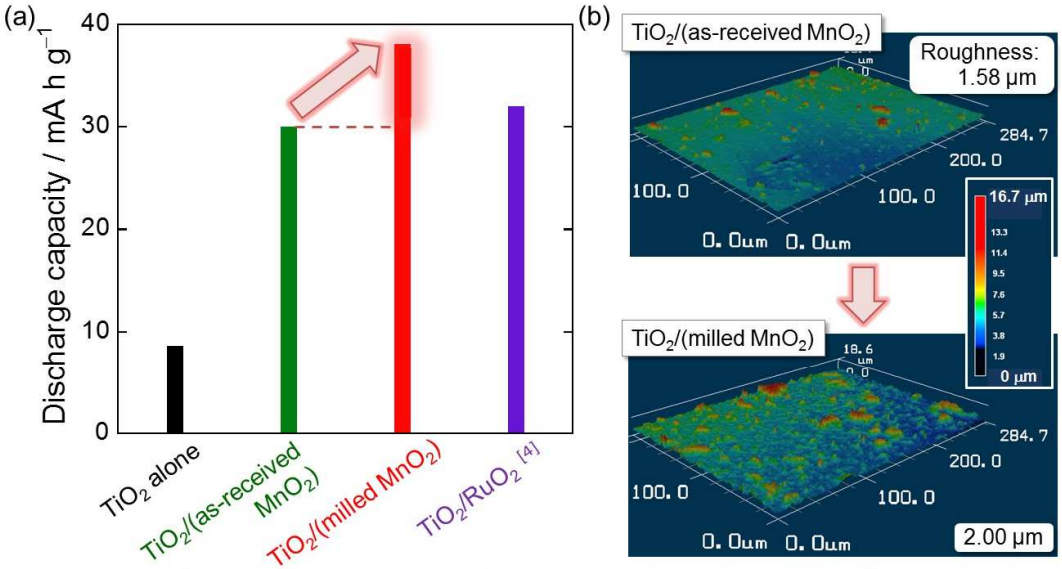

Figure 3. (a) Discharge capacities of composite electrodes of TiO_2/(as-received MnO_2) and TiO_2/(milled MnO_2). (b) Surface morphologies of these electrodes observed by confocal scanning laser microscope. By mechanical milling for MnO_2 powder, root mean square roughness of the composite electrode increased from 1.58 μm to 2.00 μm.

The difference in the capacities obviously originates from the storage/extraction of Na^+ ions into/from MnO_2 induced by the photoelectrochemical reaction, due to an insufficient photo-charge voltage of irradiated TiO_2, which is observed as a potential drop of approximately 0.3 V

(Fig. S5). Owing to this low photo-charge voltage, Na^+ ions can be stored in only near-surface regions of MnO_2 particles. We mechanically milled the MnO_2 powder to reduce its particle size, thereby enhancing the discharge capacity of the composite electrode. Figure 3(b) compares surface morphologies of the TiO_2/MnO_2 composite electrodes prepared using the as-received MnO_2 powder and the milled MnO_2 powder. The root-mean-square roughness was increased from 1.58 µm to 2.00 µm by the milling of MnO_2. As expected, the discharge capacity of the TiO_2/(milled MnO_2) electrode exhibited a higher capacity (38 mA h g^{-1}) than both the TiO_2/(as-received MnO_2) electrode and the TiO_2/RuO_2 electrode [4]. Thus, we achieved higher capacity using less expensive materials, TiO_2 and MnO_2, and this performance was attained not in two individual electrodes but in a single composite electrode.

4. Conclusions

We prepared composite electrodes comprising TiO_2 and MnO_2 particles by GD, and investigated their charge–discharge properties for photoelectric conversion and energy storage. The discharge capacity of the TiO_2/MnO_2 electrode was slightly inferior to that of electrodes composed of TiO_2 and RuO_2; however, by reducing the size of MnO_2 particles, the capacity of the composite electrode successfully enhanced. We found that the smaller MnO_2 particles can store Na^+ ions more efficiently even at a low photo-charge voltage of TiO_2.

Acknowledgements

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Figure Captions

Figure 1. Schematic illustration of measurement system for photoelectrochemical capacitor electrode.

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