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Multi-plate, thin-film electrodes of manganese oxide synthesized via the thermal decomposition of a manganese-amine complex for use as electrochemical supercapacitors

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ABSTRACT

Multi-plate, thin-film manganese oxide electrodes were synthesized via the thermal decomposition of a complex of manganese (II) formate (MnF) and triethylenetetramine (TETA) at 260 °C. These approximately 200 nm thick plates contained 50–100 nm nanoparticles and were obtained from a complex of TETA and MnF with a molar ratio of 4. A cyclic voltammetry (CV) test confirmed the pseudocapacitive properties of these multi-plate, thin-film manganese oxide electrodes. The specific capacitance of multi-plate, thin-film electrodes with a mass loading of 10 μg was calculated from a CV curve at 10 mV/s that reached 938 F/g. The specific capacitance degradation was measured via a galvanostatic charge-discharge of 0.5 mA/cm^2 and was almost stable after 1,000 cycles, which resulted in good cycle stability. Thus, an electrode of non-composite manganese oxide with high specific capacitance and good stability was obtained via a simple one-step fabrication process by thermal decomposition.

1. Introduction

Electrochemical supercapacitors are energy storage devices that show promise for use in future technologies due to a high specific capacitance, a high specific power density, and a long cycle life [1–3]. Supercapacitors currently are utilized for energy storage in hybrid vehicles, wind energy applications, medical equipment, electronic equipment, etc. [4–6]. The current development of supercapacitors has focused on advanced and reliable electrode materials that exhibit superior electrochemical performance that includes high capacitance and good reversibility. Currently, ruthenium-based electrodes fulfill the criteria for a reliable supercapacitor electrode [7]. However, ruthenium is expensive, and, as such, is not suitable for mass production. Therefore, low-cost processes and materials are necessary for supercapacitor electrodes.

Several examples of noble or transition metal oxides have exhibited supercapacitive or pseudocapacitive behavior [8–12]. Manganese oxide is a particularly attractive candidate for use as a supercapacitor electrode from among the transition metal oxides. Manganese oxide possesses a high-level specific capacitance (theoretically ~1,370 F/g), it exists in large quantities in nature, it is environmentally friendly, and it can be obtained at low cost [13,14]. However, plain manganese oxide does not achieve the level of capacitance predicted by theoretical approaches, because of poor conductivity and poor textural characteristics [15,16]. Electrodeposition has been used to fabricate porous manganese oxide films for supercapacitor electrodes [17–20]. The specific capacitance of electrodes produced using these methods ranges from 377 to 445 F/g, which remains far from the theoretical value of manganese-based electrodes. Kang et al. has reported that the specific capacitance of 2-dimensional MnO_2 is increased to 774 F/g by using soft template methods [21]. Lu et al. has reported that further increases in the specific capacitance to ~1200 F/g can be achieved by fabricating 3-dimensional Mn/MnO_2 core-shell electrodes using templates and electrodeposition [22]. Efforts have been made to improve the performance of manganese oxide-based electrodes by enlarging the specific surface area and adding binary or ternary composite materials [23–36].

Three-dimensional nanostructures of composite-based electrodes consisting of manganese oxide and one-dimensional structures such as ferrite oxide or zinc oxide nanowires/nanorods have attracted tremendous attention due to their synergic effects [26–28]. Sun et al. and Sarkar et al. have reported that nanowires or nanorods can act as the conducting scaffold in support of the active materials, and can also act as an effective channel for electron

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transport [26,27]. Another three-dimensional nanostructure of a composite-based electrode consisting of cobalt oxide, carbon nanotubes, and titanium oxide is known to improve the specific capacitance [29–31]. The functional properties of various supercapacitor electrode materials are shown in Table 1, along with the specific capacitance of each. These results confirm that the specific capacitance generated from composite electrodes is higher than that from electrodes of a single (manganese) type. However, the fabrication of a composite-based electrode involves a complicated chemical route and several materials that could increase production cost. Another method that has been used to increase the specific capacitance of a manganese oxide-based electrode has been to enlarge the specific surface area by forming an electrode with a porous structure.

Electrically conductive copper film has been fabricated by the thermal decomposition of various copper-amine complexes, and has resulted in the lowest value for resistivity by calcination with a temperature range of 140–200 °C under a nitrogen atmosphere [37,38]. The use of various types of copper-amine complexes resulted in different sizes of particles and different contact conditions of particles on the surface of thin films [39]. These methods can be used to fabricate thin-film electrodes for supercapacitors with a large specific surface area and good particle contact.

In the present study, the synthesis of a manganese oxide electrode for use in an electrochemical supercapacitor was attempted via the decomposition of a complex of manganese (II) formate and amine. A complex ink was prepared and coated onto a stainless steel substrate using a spin coater, which was then calcined under an air atmosphere. The specific capacitance and degradation of a thin film electrode with various mass loadings was measured using electrochemical methods. The morphology and microstructure of this synthesized thin-film electrode was analyzed.

2. Experimental

2.1. Synthesis of manganese oxide thin-film electrodes

A powder of manganese (II) formate dihydrate (MnF, Wako Chemical, Ltd., Japan) was used as a source of manganese. Triethylenetetramine (TETA, Wako Chemical, Ltd., Japan) was used as a complexing agent. The MnF powder and TETA was kneaded with a spatula on a glass plate at a TETA to MnF molar ratio of 4. Hexanol at a molar ratio of 0.5 to MnF was added to the MnF-TETA mixture to adjust the viscosity. Thermal decompositions of plain MnF, a MnF-TETA mixture, and a MnF-TETA-hexanol mixture were subjected to thermal gravimetric analysis (TG-DTA 6300, EXSTAR6000, SII Nano Technology Inc., Japan) to determine the calcination temperature. The atmosphere was air with a flow rate of 500 mL/min and a heating rate of 5 °C/min. A MnF-TETA-hexanol mixture was deposited onto a stainless steel substrate (SUS316, $10 \times 10 \times 5$ mm) using a micropipette, and then it was spread using a spin coater (Spin Coater 1H-DX II, Mikasa Co. Ltd., Japan) at rotating speeds that varied from 3,000 to 5,000 rpm for 1 min to control the mass loading of the thin-film electrode. The coated film was calcined using a hot plate (HP 2SA, As One Co., Japan) for 30 min under an air atmosphere. Values for the mass of the plain substrate and that of the synthesized thin-film electrode with a substrate were measured using an electronic balance (CP225D, Sartorius AG Co., Germany), and then the mass loading of the thin-film electrode onto the stainless steel was obtained based on the difference between the two.

2.2. Characterization of the electrode

A MnF-TETA-hexanol mixture was coated onto a glass substrate and calcined under the same conditions to characterize the properties of the thin-film electrodes. The morphologies of the surfaces and the cross-sections of the thin-film electrodes were observed using field-emission scanning microscopy (FE-SEM, S 5200, Hitachi, Japan). A deposited thin-film electrode was scraped to obtain some powder, and then the crystal structure of the powder was analyzed using an X-ray diffractometer (XRD MiniFlex600, Rigaku Co. Ltd.) with Cu Kα monochromatized radiation.

2.3. Electrochemical performance of the thin-film electrode

Galvanostatic charge-discharge, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) methods were conducted using a potentio/galvanostat (Compact Stat, Ivium

Table 1
Functional properties of various supercapacitor electrode materials.

Type	Structure	Functional properties	Capacitance	Ref.
MnOx single	MnO_x thin film	Large surface area, reversible redox	400–425 F/g at 5–10 mV/s	[17,19]
	MnO_2 thin film	Large surface area, reversible redox	377 F/g at 2 mV/s	[18]
	MnO_2 nanotube arrays	Large surface area, reversible redox	320 F/g at 20 mV/s	[20]
	MnO_2 2 dimension	Reversible redox and high diffusion ion into 2 nm ultrathin layer	774 F/g at 0.1 A/g	[21]
Composites	Mn/MnO_2 core-shell 3 dimension porous	Good conductivity attribute to Mn, large surface area	~1200 F/g at 5 mV/s	[22]
	ZnO@MnO_2 core-shell nanoforest	Low inner resistance	31.30 mF/cm^2	[26]
	α-Fe_2O_3/MnO_2 core-shell	α-Fe_2O_3 as current collector, highly redox materials	838 F/g at 2 mV/s	[27]
	MnO_2-NPs@CoC Nanoplatelets (NPs)	NPs/CoC provide facile ion transfer	1240 F/g at 0.5 A/g	[29]
	CNT/CNF/MnO_2	CNT/CNF provide high conductivity and large surface area	517 F/g at 5 mV/s	[30]
	MnO_2/TiO_2 porous nanosheets	TiO_2 provide particular conductive substrate	287 F/g at 1 A/g	[31]
	AuPd@MnO_2 core-shell nanopilars	High conductivity and large surface area	603 F/g at 5 mV/s	[32]
	Au/MnO_2 porous electrode	High conductivity and large surface area	1145 F/g at 50 mV/s	[33]
	CuO@AuPd@MnO_2 core-shell nanowhisker	High conductivity and large surface area	1376 F/g at 5 mV/s	[34]
	Co_3O_4@MnO_2 core-shell nanowires	Reversible redox reaction of core and shell materials	480 F/g at 2.67 A/g	[35]
	$LaMnO_3$ perovskites	Structural stability of cation arrays in perovskites for charge storage	610 F/g at 2 mV/s	[36]