Preparation and electrochemical property of manganese oxide / carbon composites

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Abstract. A novel electro-chemical capacitor was tried to synthesis by assemble carbon powder with manganese oxide using an ultra-sonication in KMnO₄ solution. (ultrasonic sample). A reference sample was prepared by same condition except for radiation of ultra-sonication (settle sample). Both ultrasonic sample and settle sample show the composite of manganese oxide and carbon. Additionally, layered manganese oxide phase was observed in the ultrasonic samples. Surface atomic ratio of Mn/C decreased corresponding with increasing of used solution volume from 25 ml to 250 ml. The composite prepared using 100ml solution was greatly affected by the ultra-sonication. On the other hand, the amount of manganese on the surface has increased with the increasing of the irradiation of energy among the ultrasonic sample. The amount of manganese deposition was almost saturated with 100 mW/cm². Cyclic voltammetry curves of the obtained composites were influenced by scanning speed. The ultrasonic sample shows higher electrical capacitance than the settle sample in various conditions.

1. Introduction

Electrochemical capacitor is recently used as a large scale device of starter for diesel-electric engines and hybrid system for electric vehicles.¹ The electrochemical capacitor shows lower energy density than the secondary battery. Energy capacitor system (ECS), that is a combination of capacitor and electric circuit, is one of the solutions to improve the disadvantage of the electrochemical capacitor.² Shortening the conducting path between the electrode and active material is one effective technique to improve the performance of secondary battery and capacitor.³ Kawaoka et al.³ used the activated carbon covered with the manganese oxide as an electrode material of the lithium-ion battery. And, high electrostatic capacitance was obtained by using this electrode under the condition of a high current density and a high-speed electrical charge and discharge. In this work, the manganese oxide/carbon composite that was consisted of manganese oxide covered on the carbon was prepared by introduced the ultrasonic wave irradiation to investigate the electrochemical performance of the resulting composite for electrochemical capacitor.

2. Experimental

2.1. Sample preparation

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Ketjen black (KB:EC-600JD(Lion)) were used for the carbon source of the starting material. KB was mixed with distilled water and dispersed using ultra-sonicator of 43 kHz. The KMnO₄ solution was added to this carbon dispersed solution under condition of 10 mM KMnO₄ solution and carbon/solution ratio was set 0.88 g/l. This solution was irradiated by ultrasonic wave of 28, 45, and 100 kHz for 0.5-24 hours. The solid was dried in 80°C oven after centrifugation and washing by distilled water, and then, manganese oxide/activated carbon composite was obtained. The reference sample was prepared as same process except for the irradiation of ultrasonic wave.

2.2. Characterization
The crystalline phases in the samples were identified by power X-ray diffractometer (XRD: XRD-6100, Shimazu) with monochromated Cu Kα radiation. Their bulk chemical compositions were determined by energy dispersed X-ray analysis (EDX: EDX Genesis, EDAX) and their surface chemical compositions were determined by X-ray photoelectron spectroscopy (XPS: ESCA-5500MT, PHI). And, the Mn contents in the solution were measured by inductively-coupled plasma optical emission spectrometry (ICP: ICP-OES Prodigy, JEOL).

2.3. Electrochemical measurement
The obtained composite powder mixed with polytetrafluoro-ethylene (PTFE) in the ratio of 10:1, and the mixed powder of 100 mg was formed like the disk of 10mmφ. Alkali salts were used as an electrolyte for a cyclic voltammetry. A potentiogalvanostat (HABF-5001, Hokuto Denko) was used for the scan of potential. Platinum and a saturated calomel electrode (SCE) were used as a counter electrode and a reference electrode, respectively. A cyclic voltammogram (CV curve) was measured under following conditions; the potential width set from -0.2 to 1.0 V and the scan rate set from 2.5 to 10 mV/s. From the CV curve, the charge-storage capacitance was calculated using the following equation

\[ Q = \int \frac{I}{dV/dt} dV \]

where I is the current density. The electrostatic capacitance (C) was estimated by C=Q/ΔV, where ΔV is the width of potential.

3. Results and Discussion

3.1. Crystalline phase of composites
Figure 1 shows the XRD patterns of the ultrasonic wave irradiated sample (Ultrasonic sample) and the sample of leaving settle (Settle sample) in various amounts of the solution. Broaden peaks around 2θ=25° and 45° were assigned as halo pattern of carbon from the KB. The peaks around 2θ=12° and 37° were assigned as manganese oxide. The peak around 2θ=12° was only observed in the Ultrasonic sample. This phase was considered to create by ultrasonic irradiation. The layered manganese oxide of Barnesite type has diffraction peak at this position. Therefore, it was shown that the manganese oxide which has high electrochemical performance was synthesized by the ultrasonic irradiation.

3.2. Chemical composition of composite
Figure 2 shows a relationship of manganese/carbon ratio of Ultrasonic sample and Settle sample by XPS and the volume of the using solution. The ultrasonic sample showed a higher Mn/C ratio than the Settle sample on all conditions. Therefore, it is thought that a selectively reduction is occurred on the surface of the carbon by the ultrasonic irradiation. From the ICP analysis, residual Mn content of the Ultrasonic sample was also less than that of the Settle sample. For preparation with 100ml solution, the Mn/C ratio between the Ultrasonic sample and the Settle sample showed the maximum difference.

**Figure 2.** Relation between amount of solution and surface Mn/C ratio of the Ultrasonic sample and the Settle sample.

**Figure 3.** Relation between energy of ultrasonic wave to solution and surface Mn/C ratio.

Figure 3 shows the relationship between the ultrasonic wave energy estimated from the amount of solution and the amount of the surface manganese. Although the amount of the surface manganese increased with increasing of irradiation energy to 100 mW/cm\(^3\), it was saturated over the irradiation energy of 100 mW/cm\(^3\).

![Graph](image1.png)

**Figure 4.** Cyclic voltammogram curves for various scan rate; (a) the Ultrasonic sample and (b) the Settle sample.

3.3. Effect of electrostatic capacitance by an electrolyte

The electrochemical property of the sample prepared with 100 ml solution was evaluated. Figure 4 shows the CV curve in 2M-KCl solution of the Ultrasonic sample and the Settle sample. In each sample, the CV curve has not changed until cycle of 10 times. When the scan rate changed fast, the shape of the CV curve changed narrow hysteresis. This change showed a decrease of the electrostatic capacitance.
capacitance. Figure 5 shows the electrostatic capacitance of each scan rate in the electrolyte of Li$_2$SO$_4$, Na$_2$SO$_4$, and K$_2$SO$_4$. The Ultrasonic sample showed higher electrostatic capacitance than the Settle sample under various scan speed and electrolyte. The maximum capacitance was about 380 F/g of the Ultrasonic sample in Na$_2$SO$_4$ or K$_2$SO$_4$ for electrolyte. The Ultrasonic sample has a Barnesite type manganese oxide, therefore, Li is easily introduced to interlayer of manganese oxide than Na and K. However, the electrostatic capacitance of the Ultrasonic sample has grown consequentially in order of Li $<<$ Na $\approx$ K. On the contrary, the electrostatic capacitance of the Settle sample has grown consequentially in order of Li $\approx$ Na $<<$ K.

In generally, the intercalation of K ion into carbon is more effective than that of other alkali ions because the size of K ion is corresponding to the layer distance in the graphite. Therefore, the contribution of KB to the electrostatic capacitance is larger than that of the manganese oxide in the Settle sample. In the Ultrasonic sample, the effect of K ion was not observed. Therefore, it is considered that the Ultrasonic sample has a structure that the surface is completely covered with the manganese oxide. As a result, manganese oxide/carbon composite, in which carbon is covered by manganese oxide, is obtained by ultrasonic irradiation under reaction.

4. Conclusion
Manganese oxide/carbon composites were successfully prepared by inducing of the supersonic treatment and the following results were appeared:

- The composite, the manganese oxide covered homogeneously on the carbon, was obtained by irradiating the ultrasonic wave of 100 kHz, and the phase of manganese oxide was assigned as Barnesite structure.
- The surface manganese amount of the Ultrasonic sample was higher than that of the Settle sample and especially remarkable difference was observed in the condition preparation using 100 ml solution.
- When the electrostatic capacitance was measured by a cyclic voltammetry, the Ultrasonic sample showed higher electrostatic capacitance than that of the Settle sample.

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