



Short communication

Capacitance improvement of supercapacitor active material based on activated carbon fiber working with a Li-ion containing electrolyte

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ABSTRACT

In an attempt to provide a favorable active material of Li⁺ supercapacitor for HEV use, we modified the surface of an activated carbon fiber felt by coating with some transition metal oxides after mild-oxidation treatment. Major source of enhancing capacitance is attributed to be due to the nano-ionics mechanism proposed by Maier and coworkers.

Cyclic voltammetry and constant current charge–discharge performance were examined for the surface modified samples in view of power capability. The oxides of Ag, Cu, Pd, and Sn were found effective to enhance the capacitance and high rate charge/discharge performance. The cycleability test was performed as well.

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1. Introduction

Hybrid electric vehicle (HEV) attracts attention in view of energy saving and reducing the amount of hazardous exhaust gas. Supercapacitor is expected to play an important role as the power source of HEV [1]. Since supercapacitor has high power capability and favorable charge/discharge cycle performance, extensive investigations have so far been conducted on it [2–6]. For HEV power source application, however, the specific capacitance is still inadequate for practical use, which triggered to initiate the study to enhance the specific capacitance of the active material. Practically attractive active material for supercapacitor is activated carbon (AC) and the improvement of the specific capacitance has been investigated in view of the physical properties by controlling pore size, the length, and the distribution [6–12].

On the other hand, chemical modification has been examined as well. Fang and Binder proposed to use an effective surfactant for the surface treatment, by which they enabled to have a good wettability between the electrolyte and the AC, resulting in an enlargement of the capacitance [13]. Kumagai and coworkers postulated the method to be applicable to carbon aeloge [14]. Oh and coworkers examined to modify with Ru on the surface of mesoporous car-

bon by impregnating the Ru complex compound into the pore and achieved to enhance the capacitance [15].

Maier and coworkers proposed a novel Li storage mechanism in the “nano-ionics” system, where additional amount of Li can be stored in the SEI region of nano-size metal oxides. Oxide of Ru was the typical example [16]. Application of this novel concept to modify the carbonaceous material having a large specific surface area is attractive. In this context, we can anticipate the capacitance enhancement phenomenon when we apply Maier’s concept to the conventional AC material. In this paper we would like to show the capacitance enhancement phenomenon on a commercially available AC. For the performance evaluation of such a new system, choice of fiber type AC (ACF) is favorable since it enables us to use no binder and no conductive additive for the test electrode preparation, where we need not to worry about on the interfering influence of these materials. In this study, the choice of the AC fiber was made a point of the electric conductivity of the ACF for the purpose of ensuring the verification of the present modification method, resulting in ignoring the important characteristics as the supercapacitor material.

Since the nano-ionics concept requires the presence of Li⁺ in the electrolyte for bringing its ability into full play, it is necessary to use a non-aqueous electrolyte containing Li salt. We used a 1:1 (v/v) mixture of ethylene carbonate and dimethyl carbonate containing 1 M LiClO₄. Use of Li salt as the electrolyte is not unusual in case of supercapacitor system, but high working voltage range can be realized for obtaining high energy power source [17–21].

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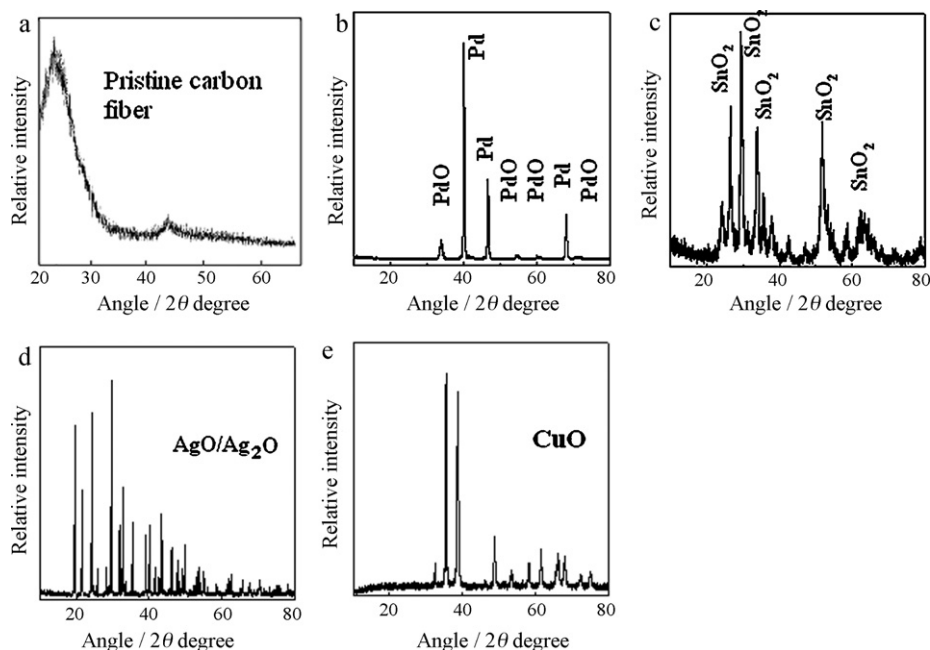


Fig. 1. XRD patterns of ACF samples with and without surface modifications. (a) Pristine sample; (b) coated with metallic Pd and PdO films; (c) coated with SnO₂ film; (d) coated with AgO and Ag₂O films; (e) coated with CuO film.

2. Experimental

2.1. Sample preparation

The AC test sample used was a carbon fiber (ACF) integrated felt (Toho Tenax, Japan FE 200) having the BET surface area of 700 m² g⁻¹. The pores consist of simple micro-pore system with the pore diameter distributed between 2.0 and 2.5 nm, the pore volume being 0.70 ml g⁻¹. The clean-up pretreatment of the as obtained sample fiber felt was done by heating it in vacuum at 200 °C for 1 h, which was used as the starting substance, after the mild oxidation treatment (MOT) [22]. MOT was performed by heating the sample covered by a sufficient amount of acetylene black (AB) in a porcelain crucible and heated in air at 400 °C for 10 min.

The surface modification treatment was done by immersing the MOT-treated fiber felt in an aqueous solution containing a high concentration of such metal salts as PdCl₂, AgNO₃, Cu(NO₃)₂, or Sn acetate, followed by boiled the solution for 30 min, and standing at room temperature for overnight. Then the fiber was taken out and rinsed with pure water in a moment, and dried and heated at 400 °C in air to form the oxide.

The surface modified felt sample was sliced into a 3 mm thick slice, cut into 1 cm × 1 cm square, sandwiched with a folded Ni expanded sheet, and spot-welded at several points of peripherals to form the test electrode.

2.2. Electrochemical evaluation

The electrochemical evaluation was done with cyclic voltammetry (CV) and constant current Li insertion/deinsertion cycle test in a 1:1 (v/v) mixture of ethylene carbonate and dimethyl carbonate containing 1 M LiClO₄ (Tomiya Chemicals) at room temperature in an argon gas filled glove box. The measurement was performed with a Hokuto-Denko HA-151 Potentio-galvanostat in the potential range between 50 mV and 2.0 V vs. Li|Li⁺.

2.3. XRD and EDX evaluations

X-ray diffraction patterns of the test material with and without coated oxide film were obtained with Cu K α radiation by a

Rigaku RINT-2000 Diffractometer before and after the electrochemical measurements. For the purpose of analyzing surface covering species Shimadzu Energy Dispersive X-ray Fluorescence Spectrometer type DX-720 was used.

3. Results and discussion

3.1. XRD and EDX patterns showing the oxides formation

At first we examined our surface modification method to verify the formation of the metal oxide film covering over the surface of AC test material. In Fig. 1 XRD patterns are shown for pristine ACF together with four surface-modified ACF samples bearing Cu, Sn, Ag, and Pd, respectively. All the patterns of the surface-modified ACFs show the presence of oxides of these elements. In case of Pd treatment, however, considerable amounts of metallic Pd are shown together with the monoxide, indicating that the partial reduction of the Pd salt took place during the heat-treatment. In contrast, Sn is shown to be fully converted into the dioxide, and Cu was fully converted to CuO. In case of Ag treatment mixture of Ag₂O and AgO was found. Thus, oxidation reaction to form oxide of each element was confirmed to be substantially attained.

Further, we could verify the formation of surface oxide by the EDX patterns of surface treated ACF samples, which are shown in Fig. 2. A sharp strong peak at the lowest energy range is due to carbon of ACF. Presence of the transition elements can be verified for all of the surface treated ACF samples. In addition, presence of oxygen can be detected at the energy position in the vicinity of carbon peak though the amount is quite much restricted. The peak height is the lowest for pristine ACF among the samples. This is the indicative of the presence surface oxygenated entities for ACF itself. Since the oxygen amount is larger for the transition metal salts treated samples than that of pristine ACF we can infer the presence of the oxides of these elements.

3.2. Cyclic voltammogram results

The results obtained with CV measurements are summarized in Fig. 3, where repeated CVs of pristine ACF and the surface modified

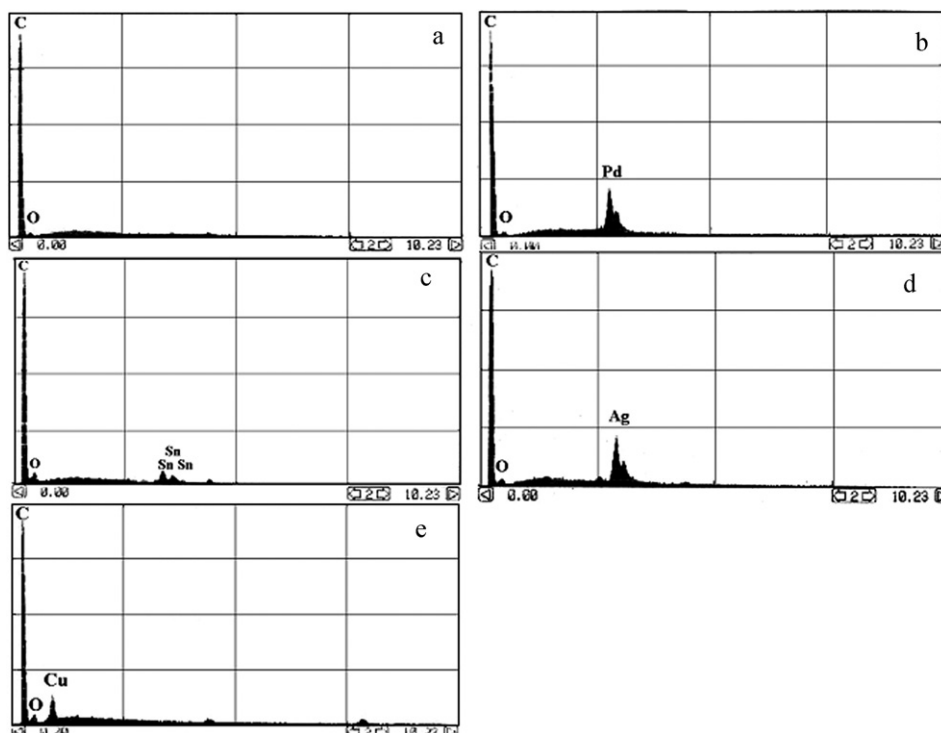


Fig. 2. EDX patterns of ACF samples with and without surface modifications. (a) Pristine sample; (b) coated with metallic Pd and PdO films; (c) coated with SnO₂ film; (d) coated with AgO and Ag₂O films; (e) coated with CuO film.

ACFs are shown. As shown on the CV diagrams the patterns were changed during cycling. The CV curves of the first scan revealed reduction peaks due to the reduction of the surface oxides and the formation of SEI in the potential range between 0V and 1.0V vs. Li|Li⁺. The sharp peaks at positive potential side are attributed to the reduction of the metal oxides, the location varying depending on the stability of the oxides. In case of surface modified samples sharp anodic peak is identified except the case of Sn, where the peak is broadened out. This anodic peak can be ascribed to the extraction

of Li, which was inserted in the SEI region caused by the nano-ionic mechanism proposed by Maier and coworkers [16]. The fact that no such peak appears on the CV of pristine sample is indicative of no deposition of metallic Li during preceding cathodic scan. After third scan the CVs tended to a stationary shape.

As shown in Fig. 3 the CV currents of the surface modified samples are quite much enlarged both on cathodic and anodic branches. This evidence shows that our idea for enhancing the capacitance was clearly attained. Fig. 4 shows an example of the CV shape

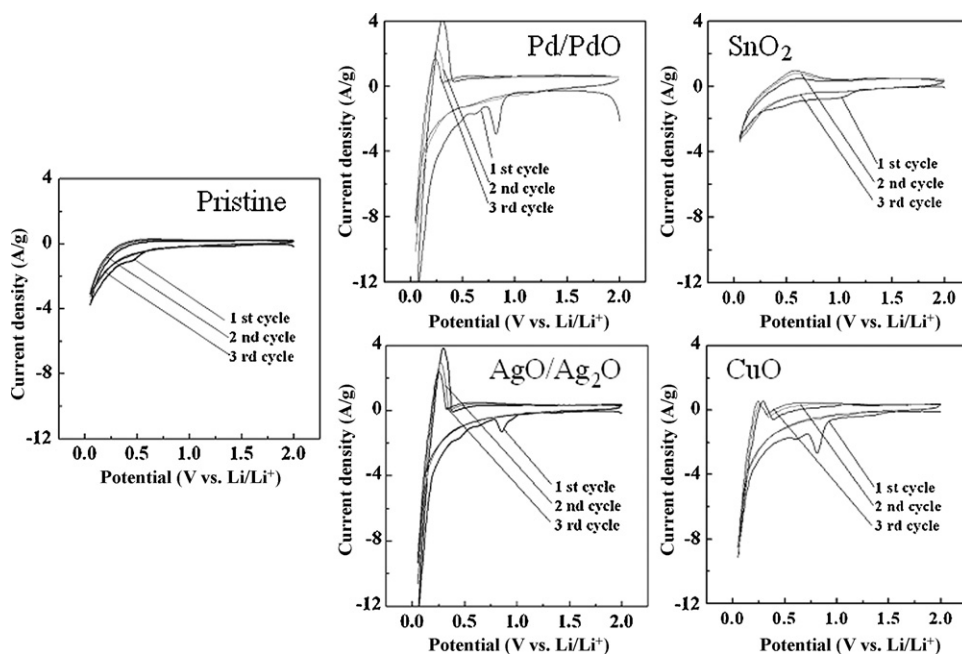


Fig. 3. CV patterns of all the ACF samples with and without surface modifications. The CV patterns were obtained with a potential scan rate of 10 mV s⁻¹ in a 1:2 mixture of EC and DMC (v/v) containing 1 M LiClO₄ at 25 °C.

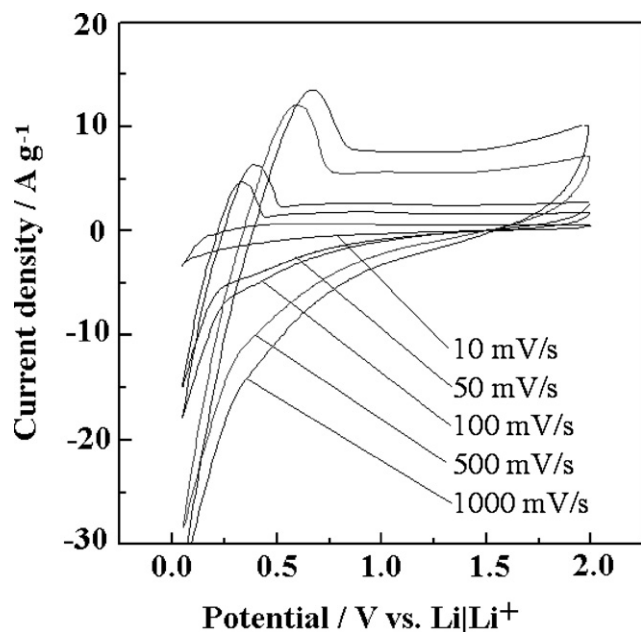


Fig. 4. CV patterns of ACF sample coated with metallic Pd and PdO films at different potential scan rates measured in a 1:2 mixture of EC and DMC (v/v) containing 1 M LiClO₄ at 25 °C.

change depending on the scan rate variation. As seen on this figure we can recognize the presence of sharp anodic peak even on the fastest scan CV. This evidence implies that the nano-ionics mechanism to store the capacitance due to Li insertion in the SEI region can respond to the rapid electrochemical action, suggesting the present method to be favorable to the application to the supercapacitor use.

3.3. Results obtained with constant current charge/discharge cycle test

In Fig. 5 the discharge curves under 10C rate constant current are summarized. The available capacitance between 0V and 2.0V is as low as 4 F g⁻¹ for pristine AC fiber sample, while in the cases

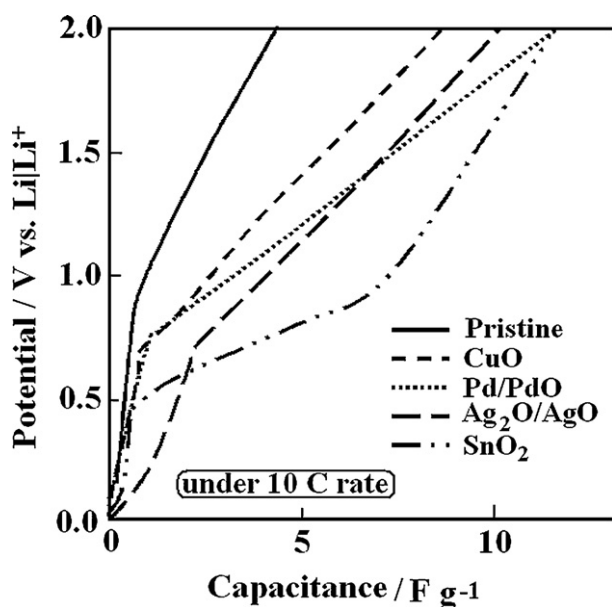


Fig. 5. Constant current discharge curves measured in a 1:2 mixture of EC and DMC (v/v) containing 1 M LiClO₄ under 10C rate at 25 °C for ACF samples with and without surface modifications.

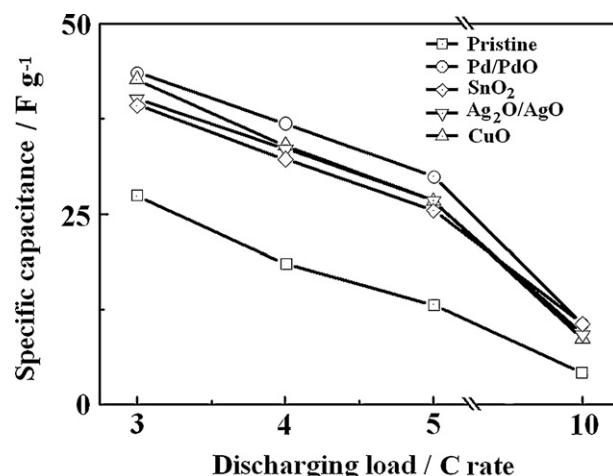


Fig. 6. High current loading rate dependency of available capacities of ACF samples with and without surface modifications for constant current discharging test in a 1:2 mixture of EC and DMC (v/v) containing 1 M LiClO₄ at 25 °C.

of Sn and Pd oxides up to three times larger capacitance could be obtained. Even in the lowest case two times larger capacitance was available for the case of Cu oxide.

The feature of the discharge curves appears to be consisting with two parts, i.e., lower potential region ranging from 0V to 0.8V, and the higher potential region up to 2.0V. In general the lines in the low potential region is a little complicated but those in the high potential region are as simple as consisting of monotonic single straight line. This appears to be due to the simple double layer charging/discharging mechanism as inferred from the CV curves shown in Fig. 3. The complicated feature in the lower potential region is ascribed to the insertion/deinsertion of Li in the SEI phase where the nano-ionic mechanism is working.

The improving effect of high rate charge/discharge capability is evidently recognized from the results shown in Fig. 6. In low current density discharging condition the available capacitance is in the region from 28 to 45 F g⁻¹, while the capacitance of pristine fiber is rapidly lowered with the increase in C rate in contrast to the case of surface modified ACF. The surface modification with transition metal oxide covering is verified to be evidently effective to keep a high capacitance even under high current density charge/discharge condition. The available capacities under different rate loadings shown in Fig 6 are summarized in Table 1, where the value decreases at high loading rate but the decreasing rate is less than that obtained with the unmodified electrode. As seen in Table 1 the available capacitance amount of the unmodified electrode at 10C rate is merely 7% of that at 1C rate, while in case of the modified electrodes the corresponding value is at least 11%, verifying the improving effect of the present modification.

The charge/discharge cycle performance of the pristine and the surface modified activated carbon fibers was examined under a heavy load of 10C rate. The results are shown in Fig. 7. As shown in

Table 1

Available capacitance measured during discharging at three different C rates for ACF samples with and without surface modifications.

Test electrode	Rate of C		
	Specific capacitance at 1.0 V vs. Li Li ⁺ (F g ⁻¹)		
	1 C	3 C	10 C
Pristine	54.2	27.3	4.0
Pd/PdO modified	85.2	49.8	12.0
SnO ₂ modified	66.6	42.6	11.5
Ag ₂ O/AgO modified	62.7	42.5	9.0
CuO modified	82.5	48.7	9.2

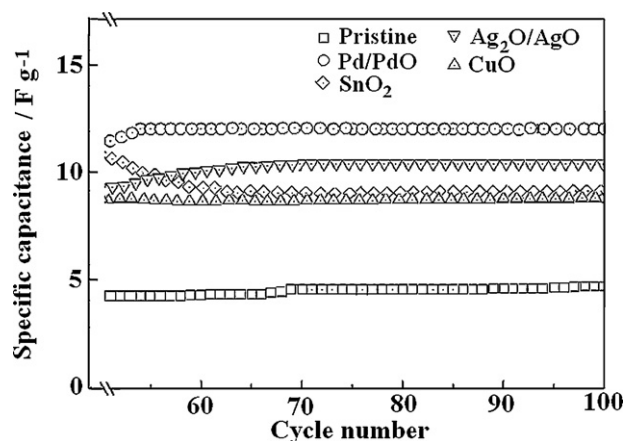


Fig. 7. Constant current charge/discharge cycling performance under 10 C rate for ACF samples with and without surface modifications. The cycling was performed in a 1:2 mixture of EC and DMC (v/v) containing 1 M LiClO₄ at 25 °C.

the figure the capacitance became steady after 70th cycle for all the samples, implying that not only the pristine sample but also all the modified samples are supposed to maintain steady discharge performance. Although a long term cycleability test over 10,000 cycles is required to guarantee the performance, results of present surface modifying method shown in Fig. 7 are considered to provide a way for contributing to the wide use of super capacitor for the power source of HEV and EV use.

The use of the electrode provided here in this work is similar to that of the negative electrode used in the hybrid type of Li-ion capacitor. It can be combined with the activated carbon cathode or the positive electrode material used in Li-ion battery, providing a large specific capacitance. Different from the negative electrode used in the conventional secondary battery system, the working mechanism of present electrode material is based on the surface red-ox reaction, therefore, the available current density for the charging and discharging reaction is quite large. This is quite suitable for the power source of HEV system.

4. Conclusions

We have been able to show that the specific capacitance for Li insertion/extraction can be enhanced by coating with transition metal oxide followed by application of electrochemical potential in an organic electrolyte containing Li⁺. This method is simple and not expensive for treatment so that we expect to be useful for practical use.

However, in this study the examinations of optimum condition have left for the future work. Therefore, hereafter we have to investigate to obtain the most favorable condition to realize the highest state.

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