

Improvement of heavy-drain discharge properties of polypyrrole cathode by the electro-codeposition of carbon powder

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Abstract

Homogeneous codeposition of polypyrrole and carbon powder was examined to obtain a cathode having more improved characteristics for lithium secondary battery. Codeposition by anodization was performed directly on a stainless-steel net from suspension of carbon powder in propylene carbonate (PC) containing 0.2 M pyrrole monomer and 1 M LiClO₄. Obtained codeposited-active materials showed favorably improved characteristics as a cathode in 1 M LiClO₄/PC electrolyte. Cyclic voltammograms of the obtained composite gave steep current peak having fairly increased height and the cathodic peak was shifted positively, indicating a reduction of the overpotential. These features imply that the codeposited material is suitable for high current charge/discharge of Li secondary battery, which was also ascertained by the constant current charge/discharge test. The capacity increase was roughly proportional to the specific surface area of the carbon powder in the deposits. Scanning electron microscopy (SEM) pictures supported the surface-enlargement mechanism for the codeposit material.

Introduction

Electroconductive organic polymers such as polypyrrole (Ppy), polyaniline, polyacetylene, polythiophene and so on, have attracted attention to the realization of practical Li secondary battery for the sake of their several suitable properties as cathode active material in nonaqueous electrolyte [1-5]. Among them, Ppy has been investigated by many authors since it has high anodic discharge voltage, fair amount of capacity, and good charge/discharge efficiency during the long-term charge/discharge cycle test [1, 5-10]. Flexibility with a good mechanical strength of the polymer is another attractive property. The capacity, however, is not favorable as compared with that of inorganic intercalating materials such as molybdenum sulfides, and oxides of manganese, titanium, vanadium, chromium, and so on. For the purpose of practical use, the characteristics of Ppy as a cathode is required to be improved to a great extent.

Attempts to improve the cathode characteristics have been made by many researchers in a different way. Fundamental research of the electropolymerization mechanism of Ppy have been carried out by several authors [7-13]. Presence of some chemical species including small amount of water in the electrolyzer was found to be effective to improve the characteristics [13-18]. Enlargement of the effective surface area of depositing Ppy has been effectively examined by several authors [19-23]. For the purpose of increasing the electric conductivity, deposition of Ppy on several types of graphite was

also examined [25]. On the other hand, composites of Ppy with some effective chemical species have been investigated to obtain favorable results to some extent [26, 27].

Although above-mentioned trials have been effective for improving the cathode characteristics of Ppy, the goal seems still ahead based on the practical use. It is well known for the battery engineers that the tight adhering of active materials to the electroconducting powder having high surface area is really effective to improve the capacity as well as the power density. Based on this concept we have attempted to prepare composite-active materials of Ppy and conducting carbon powder (Ppy-C) by the electro-codeposition technique. In this paper we will show the results thus obtained, where the cathode capacity, heavy-drain discharge characteristics, and cycleability are shown to be improved for Ppy-C obtained with a simple procedure.

Experimental

Carbon materials

Carbon blacks used were Tokai Carbon #8500, and #4500, and Nippon Carbon BP-1000. Ketjen black EC-600JD, and flake graphite powder of SP-20 were used as carbons having very high electric conductivity. The specific surface area and the particle size are summarized in Table 1. All the carbon samples were dried at 250 °C for 24 h in vacuum before use.

Pyrrrole monomer was purified by distilling Wako Junyaku reagent grade pyrrole under reduced pressure. Water free PC containing 1.0 M LiClO₄ for Li battery use was obtained from Tomiyama Yakuhin Company and used for electrolysis without any further purification.

Carbon powder of 0.06 g was suspended in 17 ml of PC electrolyte containing 0.2 M of pyrrole monomer, which was contained in a 30 ml cylindrical electrolysis cell with a separated reference electrode compartment. A 1 cm × 1 cm 50 mesh stainless-steel net was placed at the center of the electrolysis cell. A large sheet of Li foil was used as a counter electrode. Deposition of PPy or Ppy-C on the stainless-steel net was performed at constant electrolysis potential of 3.7 to 4.0 V versus Li/Li⁺ at room temperature by stirring the solution with a magnetic stirrer. The electrolysis current, however, was controlled not to exceed 10 mA to obtain a good deposit. No surface pretreatment of the carbon powder was found necessary. Total amount of charge of the deposition was controlled to 6 C per 1 cm × 1 cm stainless-steel net throughout

TABLE 1

Physical properties of carbons and corresponding cathodic characteristics of the composites obtained by electro-codeposition of carbon and polypyrrole

Product name	Average particle diameter (nm)	Specific surface area (m ² /g)	Capacity (mC/1 cm × 1 cm)	Cathodic peak current height (mA)
BP-1000	16	343	1060	51
#8500	14	290	812	38
#4500	40	60	607	22
EC600JD	30	1270	324	12
SP-20			541	24
Ppy			385	19

the preparation procedure for the carbon samples. The codeposited-active material, Ppy-C, thus obtained was then offered to reduction treatment to improve the cathode characteristics.

All the procedures were carried out in an atmosphere of a dried argon flow. Electrochemical measurements and the electrodeposition were performed with a Hokuto Denko potentiogalvanostat type HA-303 together with a Hokuto Denko function generator type HB-104 in 1 M LiClO₄/PC electrolyte at room temperature. Slow scan rate cyclic voltammetry was applied for the initial evaluation of the obtained active materials.

Scanning electron microscopy (SEM) pictures of Ppy, Ppy-C, and current collector were taken by a JEOR SEM Type JSM 5200.

Results and discussion

An example of the comparison of the cyclic voltammograms is shown in Fig. 1 for Ppy and Ppy-C (BP-1000). A remarkable enhancement of the current peak is clearly recognized for Ppy-C (full line) as compared with Ppy alone (dashed line), which is the indication of increasing effect on the capacity. Of the peak position, the cathodic peak is shifted into a positive direction, showing the possibility to realize higher discharge voltage. Steepness of the curve of Ppy-C, just before the peak, indicates that the incorporation of carbon powder is effective to reduce charge/discharge overvoltages and to offer the possibility of high current charge and discharge. This may be due to the increase of electric conductivity as well as that of effective surface area as a result of the incorporation of conductive carbon powder having high specific surface area.

If such remarkable improving effect of the cathode characteristics is due to the increase of the effective surface area of Ppy-C as suggested above, then we can expect the existence of the strong relationship between the enhancement and the specific surface area of the incorporated carbon. Intercalation of anions into the carbon particles may also contribute to a certain extent to the improvement of the total capacity.

The capacity obtained from the current-voltage curve of cathodic scan and the peak height of the peak are summarized in Table 1, where we see that the electrochemical properties are in parallel relation with the specific surface area for Ppy-C's, except Ketjen black. More clear relation between the peak current height and the specific surface area is recognized in Fig. 2. In contrast, another physical properties such as particle size or oil absorbability gave no clear relation to the capacity. These results support the above-mentioned expectation for common carbon powder. Basically, the most reasonable comparison of the capacities is to be made based on per weight of Ppy in the deposited material, but at present we have not succeeded yet to evaluate the contribution of Ppy in Ppy-C. Practically, when we compared the capacities on the basis of per weight of deposited material (total weight gain after the deposition) with those on the basis of per 1 cm × 1 cm specimen, we obtained a parallelism between them. Therefore, here we simply cite the capacities based on per 1 cm × 1 cm specimen.

Ketjen black has extremely high specific surface area, so that its use is very interesting. The results obtained, however, are far less than expected as seen in Table 1. At present the reason is not clear, but the obtained codeposit was easy to collapse, indicating loose binding between Ppy and the carbon particle, which is unfavorable as a cathode mix. Such a loose binding may be caused by the too fast local polymerization of Ppy on the very highly-active surface of the carbon.

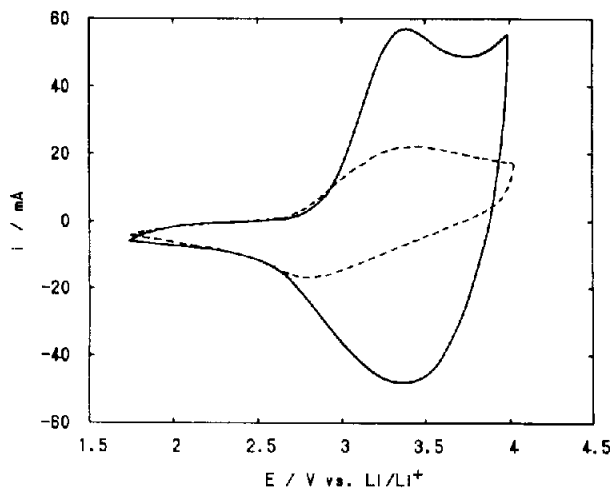


Fig. 1. Cyclic voltammograms of polypyrrole and codeposit of polypyrrole and carbon black of BP-1000 measured in propylene carbonate containing 1 M LiClO₄ at room temperature; voltage scan rate: 50 mV/sec. (—) Ppy-C (BP-1000) and (---) Ppy.

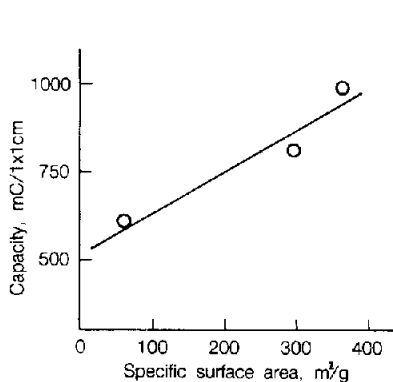


Fig. 2. Relation between the capacity and the specific surface area of carbon and the capacity of the composite of Ppy and codeposited carbon.

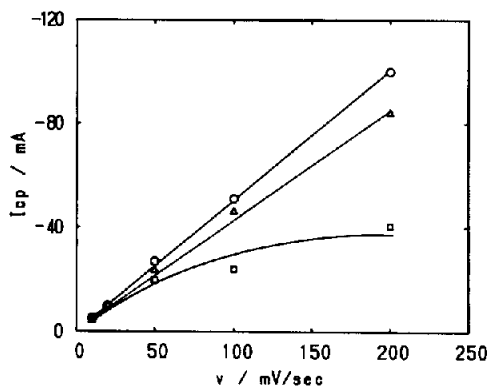


Fig. 3. Peak height of cathodic peak of cyclic voltammogram vs. voltage scan rate for Ppy and Ppy-C: (○) Ppy-C (BP-1000); (△) Ppy-C (#8500), and (□) Ppy.

Change in current-voltage characteristics depending upon the voltage scan rate was examined for Ppy and Ppy-C's, which is shown in Fig. 3. As seen in this Fig. linear relationship holds between the peak height of the cathodic peak and the scan rate for Ppy-C's of BP-1000 and # 8500, while for Ppy the peak height increase slows down with the increase of scan rate. The linear relation indicates that the electrochemical reaction is very fast, which is suitable for high current discharge. In contrast, Ppy is not suitable for the purpose. The peak current was plotted against square root of the scan rate for Ppy, which is shown in Fig. 4, where we see a linear relationship to be held. The tendency is the indication of diffusion-limited process for anion undoping. This problem of slow process has now been shown to be solved by the present method.

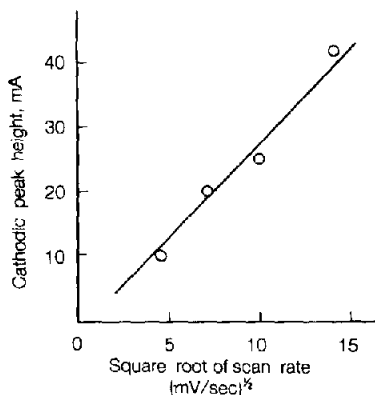


Fig. 4. Cathodic peak current height of cyclic voltammogram of Ppy vs. square root of the scan rate.

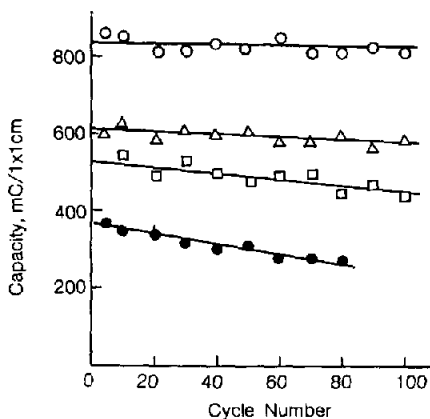


Fig. 5. Capacity of Ppy-C and Ppy vs. cycle life test in 1 M LiClO₄/PC at room temperature: (○) #8500; (△) #5500; (□) SP-20, and (●) Ppy.

Charge/discharge efficiency and cycle life were evaluated both by cyclic voltammetry and constant current charge/discharge test. Results obtained by two different methods were found in accordance with each other. The charge/discharge efficiency at the high current density test of 30 mA/1 cm² sample revealed very good value of 98 to 100%, based on the ratio of C of discharge/charge, over the range of 300 cycles for Ppy-C's, although it was lower in the initial ten cycles. The value of Ppy alone, however, was always lower than those of Ppy-C's, which may be caused by the slowness of the electrochemical reaction for Ppy.

Capacity change during the repetition of charge and discharge cycles was investigated and an example is shown in Fig. 5. It can be seen in this Fig. that the higher the capacity the more stable, and advantageous are Ppy-C's over Ppy. The improved stability may be accounted for the fast reaction rate of the Ppy-C composite.

Improved characteristics of Ppy-C are supported by the SEM pictures. In Fig. 6, SEM pictures are compared with some samples. As seen in this Fig., carbon particles in Ppy-C are well combined together by Ppy, and dispersed homogeneously over the whole Ppy matrix. Size of the primary particles of the carbon sample is as small as 10 to 30 nm, which is too small to be recognized in the picture of present magnification, therefore, particles seen in the picture are considered to be the secondary one in the Ppy matrix except for SP-20 of graphite flake, where the primary particles are large enough to be seen. Enlargement of the effective surface area of the composite can well be recognized in the picture.

Electrodeposition of Ppy has so far been investigated in detail by several authors [7-13]. In the intermediate stage, the role of oligomeric radical cation is suggested important to proceed the polymerization. Rate of dimerization of monomer radical cations formed by the electro-oxidation is considered to be slow because of their interradsical positive charge repulsion. In contrast, for oligomeric radical, the positive charge is expected to be more delocalized, so that the addition will proceed with ease as compared with the monomer radical [13]. In the presence of large amounts of carbon particles, however, even the radical monomer is considered to take part in the fast polymerization reaction if the radical is adsorbed on the conductive surface

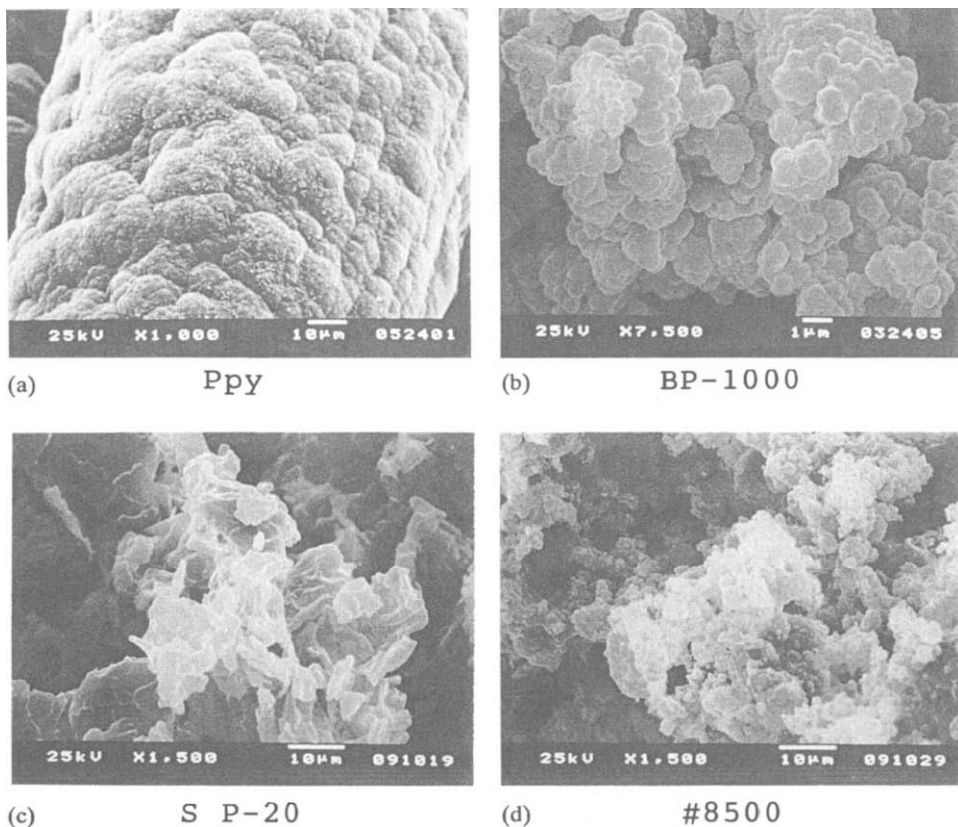


Fig. 6. SEM pictures of Ppy and Ppy-C's.

of carbon particle where the positive charge of the radical will be delocalized over the whole body of the particle. Precipitation polymerization of the oligomers is also expected to take place frequently on the carbon surface which is active for the adsorption. This implies that the polymerization of pyrrole will proceed selectively on the carbon surface and the carbon particle will then be combined together tightly through the chemical bond of Ppy.

Conclusions

Homogeneous codeposition of Ppy and carbon powder has successfully been established by a simple electropolymerization technique. Composite materials thus obtained revealed improved characteristics over Ppy as a cathode of Li secondary battery. With Ketjen black, however, we failed to obtain a composite having the expected excellent characteristics which will be attained by the investigation of an appropriate condition. The attained capacity and power density of Ppy-C's are still unsatisfactory for the purpose of realizing an excellent practical secondary battery. Based on this background, our future task will be: (i) further improvement of the power density and capacity; (ii) testing with some different electrolytes; (iii) actual test with practical battery type cell; (iv) investigation with another conducting polymer;

(v) investigation with active carbon (powder and fiber), and (vi) application to the anode.

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