Pseudo-capacitance of Activated Carbon Fiber Coated by Polythiophenes

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Electrochemical capacitors with high power and charge capacity are the most promising devices as the auxiliary power units in the fuel cell vehicle systems. There have been many reports on the improvement of the electric capacitance, or energy density, of the electrochemical capacitors. Composites of high surface area carbon materials with redox-active components will meet such a capacitance-enhancement issue. We have examined composite electrodes of polythiophenes deposited on a sheet of activated carbon fiber (ACF) for electrochemical capacitor use¹⁾. The electrochemical capacitance was significantly dependent on the preparation conditions of the composite electrodes. In the present paper, the pseudo-capacitance of the composite electrodes have been investigated in detail.

Polythiophene(pTh), poly(3-methylthiophene) (pMeT) or poly(3-methoxythiophene) (pMeOT) were deposited on the ACF substrate electrode by anodic polymerization of the corresponding thiophenes from organic media (acetonitrile: AN). The morphology of the electrode was observed by FE-SEM. The surface area and the pore size distribution were determined by a conventional gasadsorption method. The electrochemical activity of the ACF-polymer composite electrode was investigated by cyclic voltammetry and galvanostatic charge-discharge cycling.

The ACF-pTh composite electrode prepared by a usual manner gave a voltammogram with redox active current peaks that was superimposed on the double-layer capacitance of the ACF substrate. However, the deposition of the polymer tended to decrease the high surface area of the ACF substrate. Moreover, the redox activity of the polymer decreased with the repeated cycles¹.

Thus, we have modified the preparation method to improve the capacitor characteristics of the ACF-polymer composite. We examined two different processes of the eloectro-polymerization.

Method A: The ACF sheet was first immersed in an AN solution dissolving the supporting electrolyte, TEABF₄ (TEA: tetraethylammonium), under a reduced pressure, so that the pore of the ACF sheet is filled with TEABF₄/AN solution. Then, the polymerization of thiophenes (pTh, pMeT, pMeOT) was conducted in the solution containing theorresponding monomer using the TEABF₄/AN-filled ACF electrode. The resulting electrode is denoted as Type (I), ACF-pTh(I).

Method B: The ACF sheet was first immersed in an AN solution containing the monomer under a reduced pressure, so that the pore structure of the ACF was filled with the monomer solution. After that, the anodic current was applied to polymerize the adsorbed monomer in the AN solution containing no monomer. The resulting electrode is denoted as Type (II), ACF-pTh(II).

The electrode characteristics of the ACF-polymer composite were dependent not only on the polymer material but also on the preparation method. Typical voltammograms are shown in Fig. 1 for the electrodes based on poly(3-methokythiophene) (pMeOT). Broad current peaks attributed to the Faradaic reaction of pMeOT are superimposed on the double-layer charging current of ACF for Type (I) electrode, ACF-pMeOT(1). That is, ACF-pMeOT(I) has both the double-layer capacitance of ACF with pore structure and the pseudocapacitance based on the conductive polymer. On the other hand, Type (II) electrode, ACF-pMeOT(II), shows no significant increase in the Faradaic current but slight increase in the capacitive current. This result suggests that different surface structures were introduced into the ACF-polymer composites by using different preparation procedures. Similar results were obtained for the cases using different thiophenes (pTh, pMeT). The pore structure of the ACF-polymer composites examined by the gas adsorption technique proved that the poredistribution profile was modified by the polymer deposition, which was dependent on the polymerization procedure.

Accumulated capacitance measured by galvanostatic charge-discharge cycling was increased by the introduction of the conductive polymer. ACF-pMeOT(I) showed almost double of the capacitance compared to that observed for the original ACF electrode, whereas ACF-pMeOT(II) gave about 50% increase in the capacity throughout the change in the cycling current.

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REFERENCES

 M. Araki, N. Yoshimoto, M. Ishikawa, M. Morita, Extended Abstracts of 44th Battery Symposium in Japan (Paper No. 2E22), p.670 (2003).



Fig. 1 Cyclic voltammograms for ACF-pMeOT(I) (A) and ACF-pMeOT(II) (B) electrodes in 0.1 M TEAP/AN. Scan rate = 2 mV s⁻¹.