Potentiodynamically Deposited Nanostructured MnO_2 and Polyaniline-MnO_2 Composite: High Performance Electrode Materials for Redox Supercapacitors

Norio MIURA[a] and Kalakodimi Rajendra Prasad[a,b]
[a]Art, Science and Technology Center for Cooperative Research, Kyushu University, Kasuga-shi, Fukuoka 816-8580, Japan
[b]Japan Science and Technology Agency

1. INTRODUCTION

Electrochemical supercapacitors are a kind of charge-storage devices, which possess high power density, excellent reversibility and have long cycle-life compared to batteries. Supercapacitors have attracted increased interest during the last few years with projected applications, which include load leveling for batteries in hybrid vehicles, burst power generation and memory back-up devices.

Metal oxides[1,2)] and conducting polymers with various oxidation states are considered to be promising materials for supercapacitors. MnO_2 and polyaniline (PANI) are considered to be excellent materials for the above application. The aim of the present investigation is to study the capacitive characteristics of MnO_2, PANI and PANI-MnO_2 composite electrodes.

2. EXPERIMENTAL

All the materials (MnO_2, PANI, PANI-MnO_2) were potentiodynamically deposited onto an inexpensive stainless steel (SS) substrate. The area of SS used for the deposition was 1 cm^2. All potentials in the present study were measured against an SCE. MnO_2 was deposited by cycling SS between 0.5 and 1.5 V at various scan rates from an electrolyte solution of 0.5 M H_2SO_4 + 0.5 M $MnSO_4.5H_2O$.

PANI was deposited by cycling SS between -0.2 and 1.2 V at a scan rate of 200 mV s^{-1} from an electrolyte solution of 0.5 M H_2SO_4 + 0.5 M aniline. Composite electrode of PANI and MnO_2 (PANI-MnO_2) was made by first depositing PANI onto SS and then depositing MnO_2 onto PANI matrix (both at a scan rate of 200 mV s^{-1}). Various masses of all the materials were deposited and the capacitive characteristics were studied by cyclic voltammetry (CV), charge/discharge cycling in 0.1 M Na_2SO_4 electrolyte media.

3. RESULTS AND DISCUSSION

(i) MnO_2 electrode: The SEM images have indicated that the porosity of MnO_2 increases with increasing scan rate of deposition. Nanowhiskers of MnO_2 were formed at high scan rates. A large magnitude of current and rectangular type of voltammogram was obtained with MnO_2 deposited at all scan rates, indicating the capacitive behavior of MnO_2. The SC values of MnO_2 were found to increase with increasing scan rate of deposition (Fig. 1). For MnO_2 deposited at 200 mV s^{-1}, a maximum SC of 482 F g^{-1} was obtained from CV at low scan rate of 10 mV s^{-1}, and a SC value of 275 F g^{-1} was obtained even at a high scan rate of 150 mV s^{-1}, indicating a high power density of EMD. The values of SC obtained in the present study are much higher than that reported in the literature (230 F g^{-1}) at low scan rate of 20 mV s^{-1}. The SC was also found to increase with an increase in thickness of MnO_2 and the material was found to be highly stable.

(ii) PANI and PANI-MnO_2 electrodes: Nanostructured MnO_2 was deposited onto nanoporous PANI to form a nano-composite material. Symmetrical capacitors were assembled with PANI and PANI-MnO_2, and the capacitors were characterized by charge/discharge cycling at various current densities. First, a constant mass of MnO_2 was deposited on to various masses of PANI and the capacitive characteristics were studied. There is an unexpectedly large increase in SC resulting from deposition of only a small quantity of MnO_2 (0.2 mg cm^{-2}) on the surface of PANI. In the second part, various masses of MnO_2 were deposited onto a constant mass (4 mg cm^{-2}) of PANI. The SC increases with an increase in mass of MnO_2 and saturates at high masses of MnO_2. A highest SC value of 715 F g^{-1} and an energy density of ~ 200 Wh kg^{-1} were obtained (Fig. 2) at a reasonably high power density and all the electrical parameters were found to be highly stable over 5000 charge/discharge cycles. The novelty of the material, method of synthesis and high values of energy density at reasonably high values of power density are the important findings of the present investigation as well as for commercial exploitation

REFERENCES

[1] N. Miura, S. Oonishi, K. Rajendra Prasad, *Electrochem. Solid-State Lett., (2004) in press.*
[2] K. Rajendra Prasad, N. Miura, *Electrochem. Solid-State Lett., (2004) in press.*

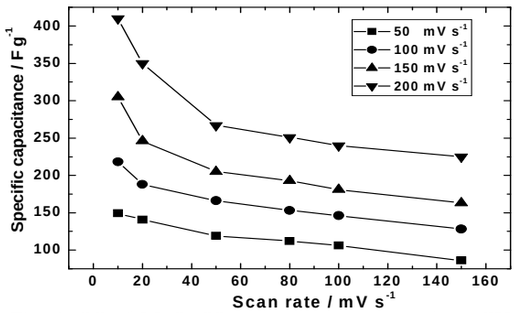

Fig. 1. SC of MnO_2/SS electrodes calculated from CV against the scan rate. MnO_2 was prepared by potentiodynamic method at various scan rates (indicated in the inset) to a mass of 0.2 mg cm^{-2}.

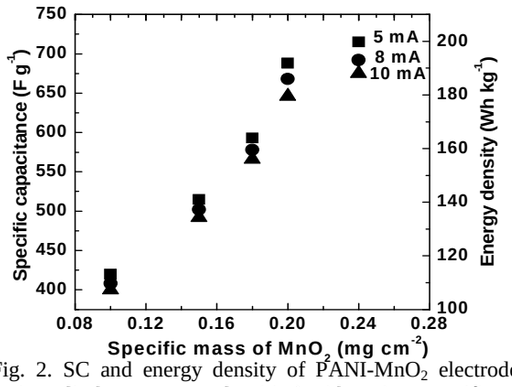

Fig. 2. SC and energy density of PANI-MnO_2 electrodes (at various discharge current densities) with various specific masses of MnO_2. The specific mass of PANI was kept constant at 4 mg cm^{-2}.