Supercapacitive properties of a nanowire-structured MnO₂ electrode in the gel electrolyte containing silica

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1. Introduction

A supercapacitor is a significant energy storage device that has attracted much attention due to its high-power capability and long cycle life, compared to conventional batteries [1]. Supercapacitors have been employed in many applications such as memory back-up in electronic devices and hybrid electric vehicles that use a fuel cell or battery [2]. Supercapacitors may be classified into carbon-based electric double layer capacitors [3–6] and conducting polymer- and metal oxide-based pseudocapacitors [7–12]. In a pseudocapacitor, the charge can be concurrently stored on the electrode surface through a double layer and in the bulk of active material via a faradic reaction. Various metal oxides, including RuO₂ [10,13], MnO₂ [14–17] and NiO, [18], have been studied to evaluate the charge storage behaviors in supercapacitor electrodes. Among the metal oxides, MnO₂ appeared to be one of the most attractive electrode materials for supercapacitors, due to its low cost, availability, environmental friendliness, and higher capacitance. However, the supercapacitive performance of a MnO₂ electrode depends on the particle size of the active material, electrode morphology, and its crystal structure. In addition, the nanostructured active material for the supercapacitor electrode is a critical issue in overcoming the intrinsically low electronic conductivity and clustered morphology of MnO₂ [14,19].

In the electrolyte system of a supercapacitor, there are three kinds of electrolytes: the liquid-type, gel-type, and polymeric solid electrolytes. The liquid electrolyte shows generally high ionic conductivity but the electrolyte leakage remains problematic. The low ionic conductivity of a solid polymeric electrolyte can reduce the performance of supercapacitors. However, compared to liquid or solid polymeric electrolytes [20], a gel electrolyte containing inorganic fillers, e.g., alumina (Al₂O₃) and silica (SiO₂), is advantageous in that there is no leakage and because it exhibits high ionic conductivity due to its thixotropic properties. In the present work, nanowire-structured MnO₂ electrodes are prepared by a chemical precipitation method and their supercapacitive properties are investigated by means of cyclic voltammetry in aqueous gel electrolytes consisting of 1 M Na₂SO₄ and fumed silica (SiO₂).

2. Experimental

Sodium dodecyl sulfate (Fluka) was used as received, and its 0.2 M aqueous solution was prepared by dissolving in 200 ml of distilled water and 0.06 mol of MnCl₂ 4H₂O (Aldrich). Then, 5 mol of H₂O₂ (Junsei, 35%) and 40 ml of ethanol were added to the as-prepared solution. After vigorous stirring for 1 h, 0.04 mol of KMnO₄
(Aldrich) aqueous solution, which has been prepared by dissolving in 50 ml of distilled water, was added to the as-prepared solution. After vigorous stirring for 3 h, the resulting brown precipitate was separated by decantation and washed several times with distilled water. Subsequently, it was dried at 40 °C under a vacuum for 12 h. A scanning electron microscope (SEM, Hitachi) and a high resolution transmission electron microscope (HR-TEM, Jeol) were employed to characterize the nanostructured morphology.

The MnO2 electrode was fabricated by mixing the prepared MnO2 (80 wt.%) as an active material with a vapor-grown carbon fiber (10 wt.%) (Showa Denko, specific surface area 13 m2 g−1, aspect ratio 67) as a conductive agent and poly(vinylidene fluoride-co-hexafluoropropylene) as a binder (10 wt.%). The electrode composite was made using N-methyl-2-pyrrolidone as a solvent. The resulting slurry was cast on a Pt foil (50 μm thick) as a current collector using a doctor blade apparatus to yield an electrode with a thickness of 60 μm. The electrodes were dried overnight and then dried under a vacuum at 60 °C for 24 h. After drying, the electrode was uniaxially pressed to enhance contact and adherence to the foil. The electrode was cut to 1 × 1 cm2 and used as a working electrode. Cyclic voltammetry was carried out using a potentiostat (EG&G, Model 273A) equipped with a three-electrode cell system. An Ag/AgCl electrode (Metrohm AG 9101 Herisau, 3 M KCl, 0.222 V vs. SHE at 25 °C) was used as a reference electrode, a coated MnO2 current collector as a working electrode, and a 2 × 2 cm2 Pt plate as a counter electrode. Cyclic voltammograms were obtained between 0.1 and 0.9 V potential windows in both the liquid electrolyte of 1 M Na2SO4 and the silica gel electrolytes. The gel electrolytes used were prepared by adding the specified amounts (0–5 wt.%) of fumed silica (SiO2) (Aerosil 200, Degussa) with a hydrophilic surface into the 1 M Na2SO4 aqueous electrolytes.

The ionic conductivity of the gel electrolytes of 1 M Na2SO4 aqueous solution containing 0–5 wt.% SiO2 was determined from complex impedance spectra measured using a frequency response analyzer (Solartron HF 1225) in a frequency range of 100 kHz to 0.01 Hz. A conductivity cell composed of two stainless steel electrodes on each side of the gel electrolyte film was used. Ionic conductivity (σ) was calculated from the bulk resistance (R) using the relation $\sigma = \frac{l}{R \times A}$, where l and A represent the thickness of the gel electrolyte film and the conductivity cell area, respectively.

3. Results and discussion

Fig. 1(a) shows the Nyquist plots for the 1 M Na2SO4 electrolyte containing various amounts of fumed SiO2. The real components of the impedance spectra at high frequency, corresponding to the solution resistance and electronic/ionic resistance of the electrode film, appeared around 10μm with slight deviations for other samples with different SiO2 contents. Fig. 1(b) shows the ionic conductivities as a function of SiO2 content in the 1 M Na2SO4, as calculated from the real components. All of the conductivity values are in a very small range between 0.125 and 0.147 S cm−1. That is to say, the gel electrolytes containing SiO2 demonstrate potentials in ionic conductivity comparable to those of the liquid electrolytes.

Fig. 2 shows SEM and HR-TEM images portraying the morphological properties of nanowire-structured MnO2. The nanowires grow completely to a well-defined length of 300–700 nm and a diameter of 10–50 nm. In the HR-TEM image, the aggregated
MnO2 species are distributed in the crosslinking points among the nanowires. The nanowire part surrounding the crosslinks has an average length above 0.8 μm and an average diameter below 10 nm. The large particles of MnO2 consist of aggregates of MnO2 primary particles, whereas the nanowire part forms numerous defects on the nanowire walls to increase the specific surface area. This nanowire-structured MnO2 active material can possess higher potentials in supercapacitive properties due to their higher specific surface area like the MnO2/activated carbon nanotube structure [21].

In order to investigate the supercapacitive properties of the nanowire-structured MnO2 in the gel electrolyte containing SiO2, cyclic voltammograms were obtained during 1000 cycles at 100 mV s\(^{-1}\) as shown in Fig. 3. The absolute current density in the cyclic voltammogram gradually increased in accordance with the increase in cyclic number until 1000 cycles. This indicates that the ionic pathways are sufficiently developed for ions to approach the electroactive sites in the bulk electrode. After 1000 cycles, both the liquid and gel electrolytes exhibit nearly rectangular shapes with a mirror image of the current response, indicating ideal capacitance behavior. However, the MnO2 electrode in the gel electrolyte with SiO2 exhibits higher current density and a better rectangular shape than those in liquid electrolyte. The specific capacitance was calculated from the cyclic voltammograms using the equation \(C = (Q_a + Q_c)/(2m \Delta V)\), where \(C\), \(Q_a\), \(Q_c\), \(m\) and \(\Delta V\) denote the specific capacitance, anodic and cathodic charges on each scan, mass of the electroactive material, and the potential window of the cyclic voltammetry, respectively. The specific capacitance values are shown in Fig. 4 as a function of cycle number. After 1000 cycles, the specific capacitance value for the MnO2 electrodes were 121 and 151 F/g in the liquid electrolyte and the gel electrolyte containing 3 wt.% SiO2, respectively. The increase and saturation in the specific capacitance with the increase in the cycle number may have resulted from the sequential activation from the surfaces of the nanowire and MnO2 aggregates into the bulk phase of the active material. This effect can also be attributed to the increase of wettability between electrolyte components caused by long-term immersion [22] or gradual penetration of the electrolyte into the bulk electrode [23].

In addition, better capacitive behavior of the MnO2 electrode in the gel electrolyte can be achieved from the hydrophilic SiO2 particles that exist in the electrical double layer. Because the surface of hydrophilic SiO2 may interact with \(H^+\), a large amount of Na\(^+\) ions can be adsorbed around the –OH groups in the water component of an aqueous electrolyte to satisfy the electron neutrality of the MnO2 during the Mn\(^{4+}/\)Mn\(^{3+}\) reversible redox process [24]. For this reason, until the SiO2 content increases up to 3 wt.%, the specific capacitance of the nanowire-structured MnO2 electrode in a gel electrolyte may be higher than that in a liquid electrolyte. When exceeding 3 wt.%, the inclusion of SiO2 particles may produce a highly viscous medium within the gel electrolyte that inhibits ion mobility by surpassing the interactions between the SiO2 surface and electrolyte species, and thereby the specific capacitance decreases. At this stage of higher SiO2 content, other key parameters such as electrode porosity and pore tortuosity should also be emphasized to determine the capacitance more accurately.

4. Conclusions

In summary, nanowire-structured MnO2 electrodes have been prepared by chemical precipitation and their supercapacitive properties have been investigated by means of cyclic voltammetry in aqueous gel electrolytes consisting of 1 M Na2SO4 and 0–5 wt.% of SiO2. The MnO2 electrode showed a specific capacitance value of 151 F/g after 1000 cycles at 100 mV s\(^{-1}\) when using the gel electrolyte filled with 3 wt.% of SiO2, which is higher than 121 F/g when using only the 1 M Na2SO4 aqueous solution. Thus, it is suggested that the nanowire-structured MnO2 electrode in a gel electrolyte with SiO2 is more suitable for use in supercapacitors.

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