



Optimization of Capacitance Balance for a Hybrid Supercapacitor Consisted of $\text{LiMn}_2\text{O}_4/\text{AC}$ as a Positive and AC Negative Electrode

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ABSTRACT :

A hybrid supercapacitor is fabricated using a composite material from LiMn_2O_4 (LMO) and activated carbon (AC) as the positive electrode and AC as the negative electrode to form the (LMO + AC)/AC system. Volume ratio (positive : negative) of electrodes is controlled to investigate of the power and energy balance. The (LMO + AC)/AC system shows better performances than the LMO/AC system. Especially, electrochemical impedance spectra, rate charge–discharge and cycle performance testing show that the (LMO + AC)/AC system have an outstanding electrochemical performance at volume ratios of (LMO + AC)/AC = 1 : 1.7 and 1 : 2. Electric double layer capacitor (EDLC) capacitance between AC of the positive electrode and AC of the negative electrode improves power density without loss of capacitance. Stable capacitance is achieved by lowering the positive electrode resistance and balancing the energy and power densities between the positive and negative electrodes by the addition of AC to the positive electrode at high current density.

Keywords : Hybrid suercapacitor, Asymmetric capacitor, Electrode volume balance, $\text{LiMn}_2\text{O}_4+\text{AC}/\text{AC}$

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1. Introduction

The demands of the electronics industry requires ever improving energy efficiency to aid the development of electric vehicles (EVs), hybrid electric vehicles (HEVs) and the miniaturizing of all portable electronic devices. Therefore, electrical energy storage devices need both high power and energy density. The lithium-ion battery^{1,2)} and the supercapacitor^{3,4,5)} have been often employed as these electrical energy storage devices. However, neither combines all desired properties: the former has higher energy density, but lower power density and cycle life compared with the latter which has complementary properties. Therefore, if supercapacitors were to have increased energy density, they would have the ideal combination of attributes.

Hybrid supercapacitors have been studied to optimize their electrochemical performance. They have been improved through the use of hybrids with electrodes of LiMn_2O_4 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$ etc. in chemical intercalation and deintercalation reactions in lithium-ion batteries and activated carbon electrodes for physical adsorption and desorption in supercapacitors.^{6,7,8)} However, hybrid supercapacitors have two problems: the balance problem of power density differences between positive and negative electrode; and also the technical problem by the energy density differences between them. Thus, lithium transition metal oxides are difficult to coat very thinly due to a large particle size and an activated carbon electrode is difficult to coat thickly because of the problem of exfoliation between the current collector and active material.

In this paper, we use a composite material from LiMn_2O_4 (LMO) and activated carbon (AC), as the composite positive electrode, and then assembled a device with AC negative electrode to form the (LMO + AC)/AC system in order

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to solve the problems of hybrid supercapacitors. The power density of the positive electrode and overall electrochemical performance were improved by AC addition to the positive electrode and control of electrodes' relative volumes.

2. Experimental

The positive electrodes were prepared with LiMn_2O_4 (Phoenix PDE, Korea) and activated carbon (RP20, Japan). The negative electrode was prepared with activated carbon. Conductive additive and binder were used in all electrodes, they were Super-P black (MMM, Belgium) and polytetrafluoroethylene (PTFE D-60, Daikin, Japan), respectively. Ethanol (Samchun chemical, 99.9%) was the dispersion medium. The quantitative materials were mixed in a three dimension mixer and stretched by a heated roller press. The electrodes were prepared as rubber types. A precision roll press controlled the electrodes' thicknesses for the experiment. Composition and thickness of electrodes are shown in Table 1. The prepared electrodes were dried at 150°C for 12 h to remove water. The positive and negative electrodes of 12 mm diameter were punched from the rolled product. The electrochemical tests were carried out using a coin-type cell (CR-2016) consisting of an anode, a separator (NKK, TF4035, Japan), and a cathode. The coin cell was assembled in an argon-filled glove box. The electrolyte was 1 M LiBF_4 and 1 M TEABF₄ in acetonitrile (AN). The rate capabilities and cycle performances of the hybrid supercapacitors were tested on a battery tester (Maccor series 4000, USA). Cycle performance tests were carried out in constant current mode (CC mode) and constant current-constant voltage mode (CC-CV mode). For each cycle, it was charged with constant current (1 mAcm^{-2}) to 2.7 V and with constant voltage at 2.7 V until charge current declined to 0.5 mAcm^{-2} . It was then discharged to 1.0 V at a constant current (1 mAcm^{-2}). Cyclic voltammograms and impedance spectroscopy

of the cells were characterized using a potentialstat (EC-Lab, France). Cyclic voltammetry was done using a scan range of 1.0~2.7 V at a scan rate of $1\sim 100 \text{ mVs}^{-1}$ for 5 cycles. Electrochemical impedance spectroscopy (EIS) was recorded by applying a low amplitude voltage of 5 mV root mean square to the system at its open circuit potential at frequencies from 100 kHz to 100 mHz.

3. Results and Discussion

Capacitance testing was carried out at a current density of 1 mAcm^{-2} from 1.0 to 2.7 V to evaluate charge/discharge performances for the LMO/AC and the (LMO+AC)/AC system. The specific capacitances of the cells were calculated by the following the equation from the discharge profile: $C = I \cdot (T_2 - T_1) / (V_1 - V_2) \cdot (X)$, Where V_1 and V_2 are 2.16 V and 1.08 V, respectively, I is 1.13 mA and X is the weight or volume sum of each electrodes. Fig. 1 shows capacitance per weight and volume, retention ratio of LMO/AC and (LMO + AC)/AC system at various volume ratios of the positive and negative electrode. The specific capacitances increased gradually with increasing volume ratio in all systems. But, capacitance faded rapidly during cycling at equal volume ratio (LMO/AC = 1 : 1). In the whole reaction of full cell, the negative electrode (AC) is fully charged before the positive electrode (LMO) is not yet charged because energy density of LMO is generally greater than that of AC. Consequently, the negative electrode was overcharged to maintain the cell voltage and the cell deteriorated by gas generation.^{9,10)}

In contrast, (LMO + AC)/AC system did not show great loss of capacitances at all the volume ratios. Even the cell with electrodes of equal volume ratio ((LMO + AC)/AC = 1 : 1) did not deteriorate greatly. The reason was that overcharge of the negative electrode was moderated because decrease of the energy density by AC addition to positive electrode. Especially, the (LMO + AC)/AC system shows outstanding electrochemical performance at volume ratios 1 : 1.7 and 1 : 2 despite decrease of LMO. This indicates that the lack of power density of the positive electrode is compensated for EDLC (Electric Double Layer Capacitor) capacitance between cathode and anode by AC addition to the cathode. Fig. 2 shows EDLC capacitance during charge at the low voltage range (0.1~0.8 V).

Fig. 3(a) and (b) show the cyclic voltammograms (CVs) of LMO/AC and (LMO + AC)/AC at volume ratio 1 : 1.7, respectively. Similar profiles of CVs were obtained with both systems. But, it shows how power density of the positive electrode is affected by AC addition to the positive

Table 1. Formulation of electrodes tested

| Electrode | Active material | Conductive additives | Binder | Thickness |
|-----------------|--|----------------------|--------------|---------------------------|
| Positive LMO | LiMn_2O_4 91.7% | Super-P 5% | PTFE 3.3% | 150 μm |
| Positive LMO+AC | LiMn_2O_4 80% + AC 11.7% | Super-P 5% | PTFE 3.3% | 150 μm |
| Negative AC | AC 90% | Super-P 5% | PTFE 5% | 150~ 350 μm |

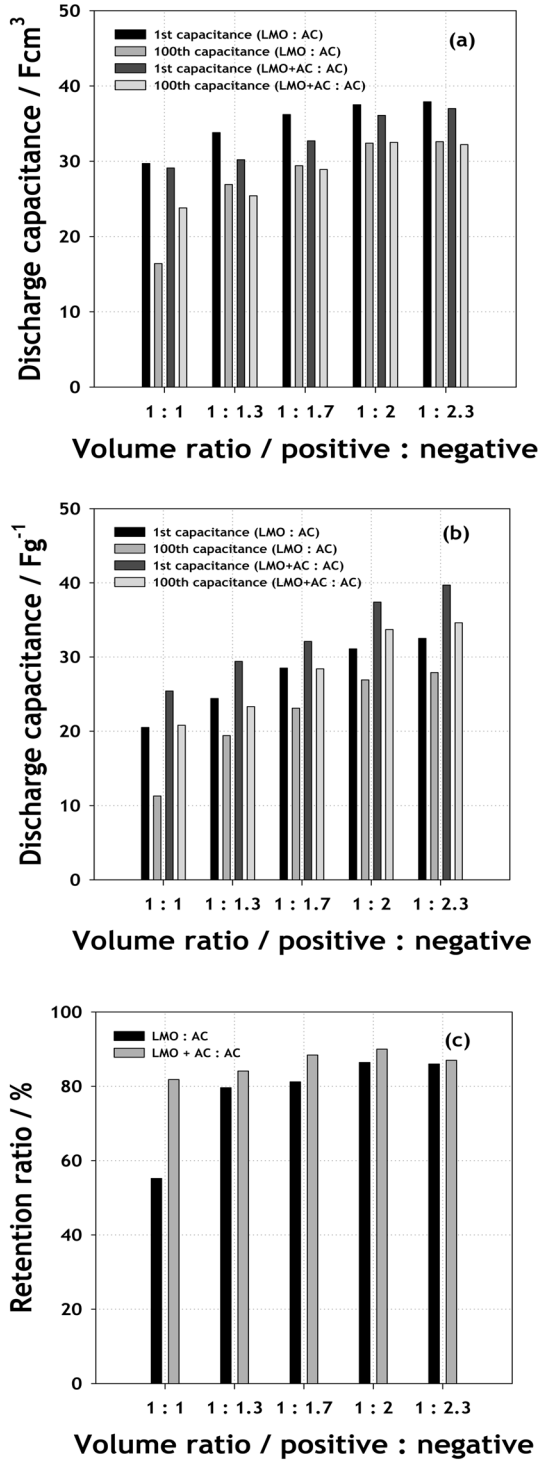


Fig. 1. The capacitances (a) per volume and (b) weight, (c) retention ratio of LMO/AC and (LMO + AC)/AC system at 1 mAcm^{-2} .

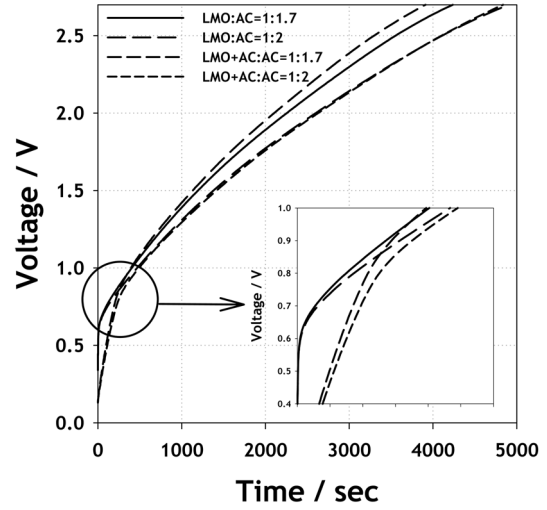


Fig. 2. Charge profile of LMO/AC and (LMO + AC)/AC systems at a current density 1 mAcm^{-2} .

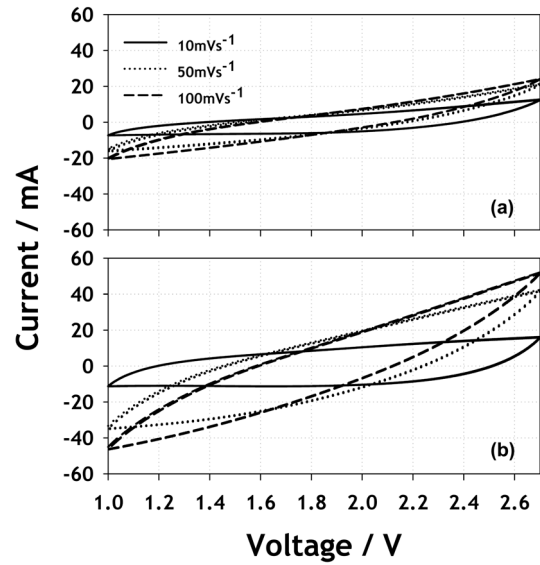


Fig. 3. Cyclic voltammograms of (a) LMO/AC and (b) (LMO + AC)/AC systems at scan rates of 10 to 100 mVs^{-1} in the voltage range of 1-2.7 V.

electrode at the scan rate of $10\sim 100 \text{ mV s}^{-1}$. It is clear that the electrochemical performance of the (LMO + AC)/AC system is superior to that of the LMO/AC system with increasing a potential scan rate. It is evidenced that AC addition to the positive electrode can balance the energy and power density difference between the electrodes of the hybrid supercapacitor.

Fig. 4 shows the variation of specific volumetric capacitance with increasing current density. When current density is increased, the specific capacitance of the (LMO + AC)/AC system shows much difference from the LMO/AC system because of the difference in power capability. At a current density of 1 mA cm^{-2} , both systems show similar capacitance. (29.4 F cm^3 for LMO/AC and 28.9 F cm^3 for (LMO + AC)/AC system) But, when the current density increases to 10 mA cm^{-2} , the capacitance difference is clear with the LMO/AC and (LMO + AC)/AC systems having capacitances of 14.9 F cm^3 and 23.5 F cm^3 respectively. Generally, hybrid supercapacitors have improved energy density compared with EDLC capacitors but power density is sacrificed instead. However, this disadvantage is compensated by AC addition to the positive electrode and control of volumetric balance between the electrodes.

EIS measurements were conducted to calculate the equivalent series resistance (ESR) of the LMO/AC and (LMO + AC)/AC system. Fig. 5 shows that a single semi-circle appears at high frequency followed by an inclined straight line for the two systems. The high frequency semi-circle represents the impedance due to a solid-state interface layer formed on the surface of the electrode; the inclined straight line at lower frequency is related to a combination of the diffusion effects of ions on the interface between electrodes and electrolyte.¹¹⁾ The ESR of the LMO/AC system at high frequency was 18.8Ω . By contrast, the ESR of the (LMO + AC)/AC system at the same frequency

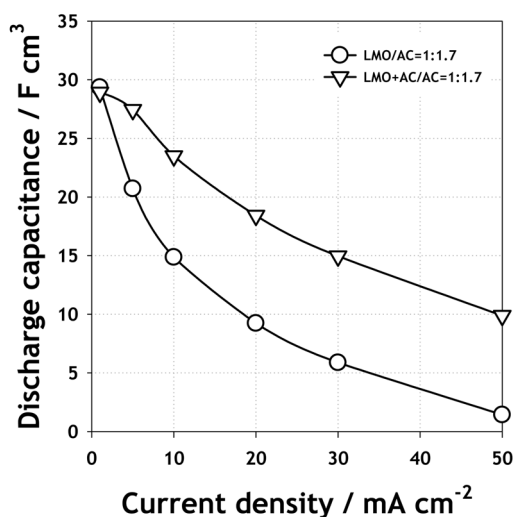


Fig. 4. Variation of capacitance with increasing current density of LMO/AC and (LMO + AC)/AC systems.

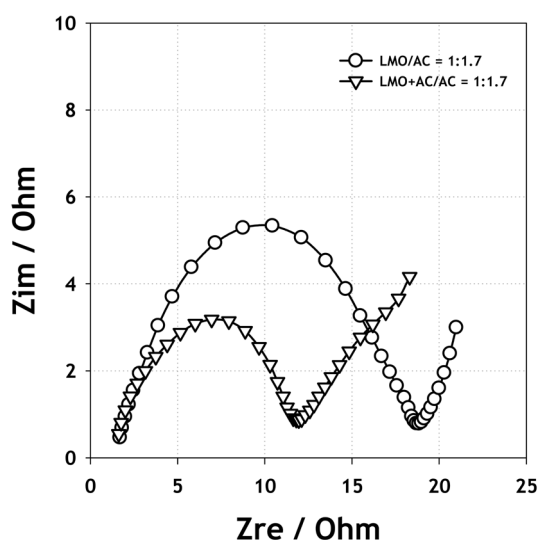


Fig. 5. Impedance spectra of LMO/AC and (LMO + AC)/AC systems at 100 kHz-100 mHz.

was only 12.3Ω . The resistance decreased as a result of highly conductive AC addition. This decrease of electrode resistance diminishes the voltage damage of the negative electrode at high current and is considered a major contributor to the improvements of product life and reliability.

4. Conclusions

A hybrid supercapacitor was manufactured using a composite of LiMn_2O_4 (LMO) and activated carbon (AC), as the positive electrode, and AC as the negative electrode to form the (LMO + AC)/AC system. The system showed improved performances of high rate capability, high specific capacitance and long life cycle performance. Addition of AC to the positive electrode could lower the resistance, reduce the weight of the positive electrode and exploit EDLC capacitance of AC/AC system compensating for lacking power density of LMO/AC system. As a result, (LMO + AC)/AC systems having the specific volumetric capacitances of 32.7 F cm^3 and 36.1 F cm^3 and retention rate could reach 88.4% and 90.0 %, respectively at optimal volume ratio of (LMO + AC)/AC = 1 : 1.7, 1 : 2. Finally, addition of AC to the positive electrode is believed to be an innovative technology which can improve the electrochemical performances of the LMO/AC system.

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References

1. R. J. Gummow, A. de Kock and M. M. Thackeray, *Solid State Ionics*, **69**, 59 (1994).
2. Y. Xia, N. Kumada and M. Yoshio, *J. Power Sources*, **90**, 135 (2000).
3. K. W. Chang, Z. Y. Lim, F. Y. Du, Y. L. Yang, C. H. Chang, C. C. Hu and H. P. Lin, *Diamond Relat. Mater.*, **18**, 448 (2009).
4. T. Morimoto, K. Hiratsuka, Y. Sanada and K. Kurihara, *J. Power Sources*, **60**, 239 (1996).
5. H. Nakagawa, A. Shudo and K. Miura, *J. Electrochem Soc.*, **147**, 38 (2000).
6. G. Glenn and Amateuei, *J. Electrochem. Soc.*, **148**, A930 (2001).
7. R. Kotz and M. Carlen, *Electrochim. Acta.*, **45**, 2483 (2000).
8. X. Hu, Z. Deng, J. Suo and Z. Pan, *J. Power Sources*, **187**, 635 (2009).
9. J. Li AND F. Gao, *J. Power Sources*, **194**, 1184 (2009).
10. S. Ishimoto, Y. Asakawa, M. Shinya and K. Naoi, *J. Electrochem Soc.*, **156**, A571 (2009).
11. Z. R. Zhang, H. S. Liu, Z. L. Gong and Y. Yang, *J. Power Sources*, **129**, 101 (2004).