



Short communication

## Electrochemical performance of carbon-coated lithium manganese silicate for asymmetric hybrid supercapacitors

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## ABSTRACT

Nanoscale carbon-coated  $\text{Li}_2\text{MnSiO}_4$  powder is prepared using a conventional solid-state method and can be used as the negative electrode in a  $\text{Li}_2\text{MnSiO}_4$ /activated carbon (AC) hybrid supercapacitor. Carbon-coated  $\text{Li}_2\text{MnSiO}_4$  material presents a well-developed orthorhombic crystal structure with a  $Pmn2_1$  space group, although there is a small impurity of MnO. The maximum specific capacitance of the  $\text{Li}_2\text{MnSiO}_4$ /AC hybrid supercapacitor is  $43.2 \text{ F g}^{-1}$  at  $1 \text{ mA cm}^{-2}$  current density. The cell delivers a specific energy as high as  $54 \text{ Wh kg}^{-1}$  at a specific power of  $150 \text{ W kg}^{-1}$  and also exhibits an excellent cycle performance with more than 99% columbic efficiency and the maintenance of 85% of its initial capacitance after 1000 cycles.

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### 1. Introduction

Electrochemical capacitors (ECs) as energy storage devices are garnering much attention due to their higher specific power relative to batteries and conventional capacitors. Such ECs have been widely used in many electric applications, including uninterruptible power supplies, portable devices, hybrid electric vehicles (HEVs), and fuel cells [1,2]. Recently, many studies have focused on asymmetric hybrid supercapacitors that possess increased specific energy over electrochemical capacitors. It is well known that a useful approach to develop hybrid supercapacitors is the transition from a capacitor-type electrode to a battery-type. Both the increase in the working voltage and the high specific energy of the battery material result in a significant improvement in the overall specific energy of the supercapacitors. Currently, many research groups have reported that fabrication of hybrid capacitors with a lithium metal oxide as the cathode is drawing increased interest given their high specific energy [3–5].

Among them, silicate-based cathode materials ( $\text{Li}_2\text{MSiO}_4$ ,  $\text{M} = \text{Fe, Mn}$ ) for lithium-ion batteries have recently generated much attention given their intrinsic stability and natural abundance [6,7]. In the case of  $\text{Li}_2\text{MnSiO}_4$ , the extraction of more than one lithium

ion is possible and results in the higher Mn oxidation state ( $\text{Mn}^{4+}$ ) that favours formation of the  $\text{Mn}^{\text{IV}}\text{SiO}_4$  phase during the delithiation process. Provided that the structure of this compound is stable, a reversible exchange of up to two lithium ions per formula unit (exploration of  $\text{Mn}^{\text{II}}/\text{Mn}^{\text{III}}$  and  $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$  redox couples) would become possible. To date, few studies have reported the utilization of  $\text{Li}_2\text{MnSiO}_4$  as a positive electrode material in lithium secondary batteries [6,7]. In fact, no proper optimization has been reported for the synthesis of  $\text{Li}_2\text{MnSiO}_4$ , which leads to debatable results. For example, Kokalj et al. [8] reported a discharge capacity that exceeded  $200 \text{ mAh g}^{-1}$  but was observed sporadically, as well as poor cycle-life. By contrast, Liu et al. [9]  $\text{Li}_2\text{MnSiO}_4/\text{C}$  electrodes exhibited a discharge capacity of only around  $125 \text{ mAh g}^{-1}$ . In this context, we have optimized the appropriate synthesis conditions for  $\text{Li}_2\text{MnSiO}_4$  by a solid-state route and obtained good cycle-life.

It is also well known, however, that  $\text{Li}_2\text{MnSiO}_4$  material requires more intensive study before being adopted as a cathode material for practical lithium-ion batteries, due in part to the low practical capacity and very poor cycleability over the full working voltage region (4.8–1.5 V). Therefore, we have focused on one interesting factor of  $\text{Li}_2\text{MnSiO}_4$  material that shows excellent cycle retention in the lower voltage region (0–3 V), even though the discharge capacity is very small and not acceptable for lithium secondary batteries. To our best knowledge, no other work has reported upon the utilization of lithium transition metal silicates as electrode materials for supercapacitor applications.

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This study reports the development of  $\text{Li}_2\text{MnSiO}_4$  as a negative electrode in a  $\text{Li}_2\text{MnSiO}_4$ /activated carbon asymmetric hybrid supercapacitor (LMS/AC) with a 1.0 M  $\text{LiPF}_6/\text{EC}:\text{DMC}$  electrolyte system.

## 2. Experimental

Carbon-coated  $\text{Li}_2\text{MnSiO}_4$  (LMS) material was prepared by a conventional solid-state method. High-purity  $\text{LiOH}$  (Junsei, Japan),  $\text{MnCO}_3$  (Aldrich, USA), and  $\text{SiO}_2$  (Junsei, Japan) were used as starting materials. Adipic acid ( $\text{C}_6\text{H}_{10}\text{O}_4$ , Dae-Jung, Korea) served as a carbon source (0.2 mol against the total metal ions present in the compound). Stoichiometric amounts of starting materials with adipic acid were ground and heated at  $400^\circ\text{C}$  for 4 h in air. After cooling down to room temperature, the mixture was ground and finally calcined at  $900^\circ\text{C}$  for 12 h under an argon atmosphere. The carbon content of the resulting carbon-coated  $\text{Li}_2\text{MnSiO}_4$  material (0.52 wt.%) was determined with an elemental analyzer (CHN Flash EA series, CE Instruments, Italy). The crystalline structure of the prepared  $\text{Li}_2\text{MnSiO}_4$  was studied by X-ray diffractometry (XRD, Rint 1000, Rigaku, Japan) with  $\text{Cu K}\alpha$  as a radiation source. Brunauer, Emmett, and Teller (BET) measurements of surface area were conducted with a micromeritics ASAP 2010 surface analyzer (Micromeritics, USA). The respective specific surface area of the  $\text{Li}_2\text{MnSiO}_4$  and activated carbon is  $0.282$  and  $1676 \text{ m}^2 \text{ g}^{-1}$ , respectively.

The electrochemical performance of the hybrid supercapacitor was studied in the form of an assembled CR 2032 coin-type cell. The positive electrode was prepared by mixing 70 wt.%  $\text{Li}_2\text{MnSiO}_4$ , 20 wt.% ketjen black (KB) as the conductive additive, and 10 wt.% Teflonized acetylene black (TAB) as the binder. This was then pressed on a  $200 \text{ mm}^2$  stainless-steel mesh that acted as the current collector. The negative electrode was prepared by the same method; it consisted of 75 wt.% activated carbon, 15% KB, and 10 wt.% TAB. The mass ratio of the cathode to anode was approximately 1:2. The LMS/AC cell was assembled within an argon-filled glove box and was composed of a  $\text{Li}_2\text{MnSiO}_4$  cathode, a porous polypropylene separator (Celgard 3401), and an AC anode in 1.0 M  $\text{LiPF}_6/\text{EC}:\text{DMC}$  (1:1 v/v) electrolyte. Cyclic voltammograms of the LMS/AC cell were obtained with an electrochemical analyzer (SP-150, Bio-Logic, France). Galvanostatic charge/discharge experiments were carried out between a cell voltage of 0–3 V and at a current density of  $1 \text{ mA cm}^{-2}$  using a cycle tester (WBCS 3000, Won-A-Tech, Korea).

## 3. Results and discussion

The XRD pattern of the prepared LMS power is shown in Fig. 1. The peaks are assigned to the  $\text{Li}_2\text{MnSiO}_4$  phase, which has an orthorhombic crystal structure with a  $Pmn2_1$  space group [10]. Additional peaks are observed in the diffractogram and identified with  $\text{MnO}$  (ICSD-76086). There are also some low-intensity peaks which possibly originate from the presence of Li and Mn silicate, as reported by several other research groups [11,12].

Cyclic voltammograms (CVs) for the LMS/AC cell recorded at different scan rates are presented in Fig. 2. This analysis is an effective tool to investigate the ideal capacitive behaviour of electrochemical systems. All curves exhibit rectangular, mirror-like images with respect to the zero-current line, as well as a rapid current response on voltage reversal at each end-potential. This implies that the hybrid supercapacitor cell exhibits a typical capacitive performance in the potential window of 0–3 V. The CV curves show that the potential difference between the peaks increases with scan rate and thereby indicates the presence of electric polarization phenomenon. Upon increasing the scan rate, these phenomena

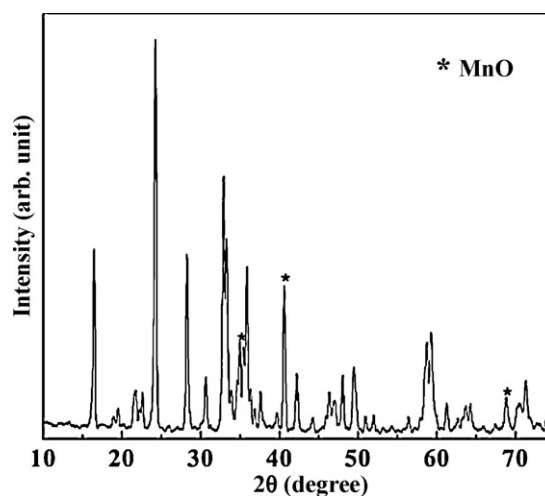


Fig. 1. XRD pattern of as-prepared  $\text{Li}_2\text{MnSiO}_4$  material at  $900^\circ\text{C}$ .

became more serious. The possible energy storage mechanism of the LMS/AC is as follows. The AC cathode forms double-layers to store energy while the  $\text{Li}_2\text{MnSiO}_4$  anode exploits the intercalated/extracted  $\text{Li}^+$  ions to produce pseudocapacitance and realize the storage of energy. During the charge process,  $\text{Li}^+$  ions are extracted from the  $\text{Li}_2\text{MnSiO}_4$  electrode and adhere on the surface of the AC *via* the electrolyte, to generate an electrochemical double-layer. On discharge, the  $\text{Li}^+$  ions de-adsorb from the AC surface and intercalate into the  $\text{Li}_2\text{MnSiO}_4$  electrode *via* the electrolyte.

Galvanostatic charge/discharge curves for the LMS/AC cell at a constant current density of  $1 \text{ mA cm}^{-2}$  between 0 and 3 V are given in Fig. 3(a). The discharge profile generally consists of three parts, namely: a small voltage drop (IR drop) due to the internal resistance; a double-layer region due to ion separation at the electrode|electrolyte interface; the redox component attributed to the charge-transfer reaction of the  $\text{Li}_2\text{MnSiO}_4$  battery material in the longer time region. The results show that the hybrid system is a combination of double-layer capacitor and battery characteristics. It can be seen from the charge/discharge curves that the potential linearly varies with time during charge and discharge with a constant slope for the charge/discharge curves. The curves have a symmetrical trilateral shape and thereby reveal that the LMS/AC cell has excellent cycle performance and high electrochemical reversibility. A specific capacitance ( $C_s$ ) of  $43.2 \text{ F g}^{-1}$  is obtained at a  $1 \text{ mA cm}^{-2}$ . Fig. 3(b) shows that this hybrid supercapacitor has

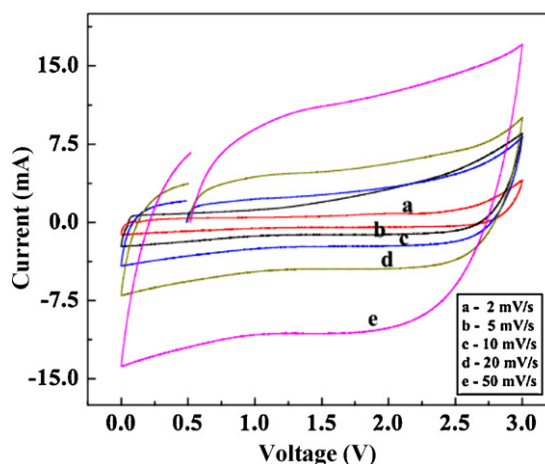
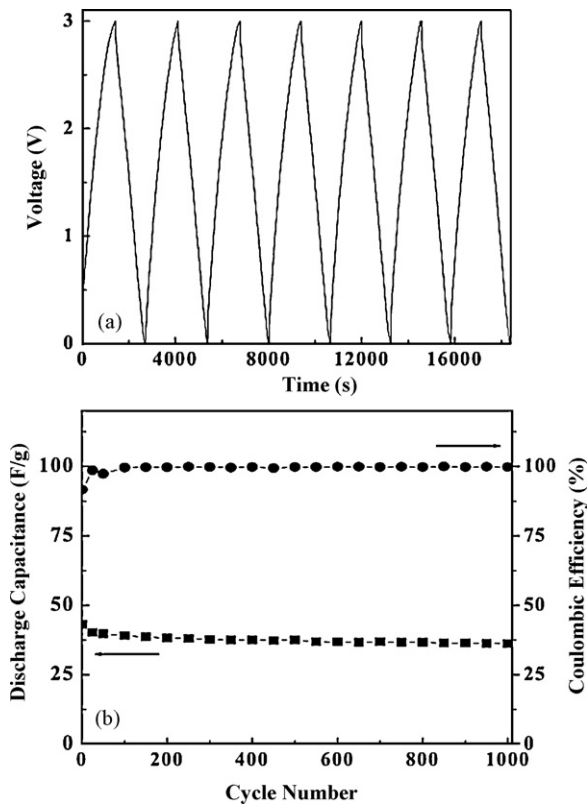


Fig. 2. Cyclic voltammogram for LMS/AC cell at different scan rates.



**Fig. 3.** (a) Charge/discharge curves of LMS/AC cell; (b) discharge capacitance and coulombic efficiency as a function of cycle numbers at a  $1 \text{ mA cm}^{-2}$ .

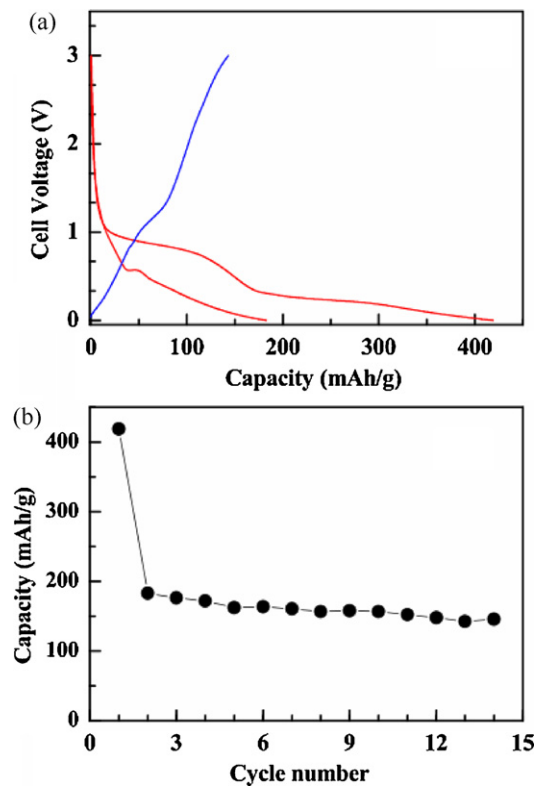
an excellent cycle-life with a specific capacitance that is maintained at more than 85% of its initial value after 1000 cycles. The coulombic efficiency ( $\eta$ ) of the LMS/AC cell is also shown in Fig. 3(b): it was calculated according to the equation:  $\eta = (\Delta t_D / \Delta t_C) \times 100$  where,  $\Delta t_D$  and  $\Delta t_C$  are the discharge and charge times, respectively. The hybrid cell shows a very stable efficiency of greater than 99%, even after 1000 cycles.

For comparison, the electrochemical performance of  $\text{Li}_2\text{MnSiO}_4$  vs. lithium reference electrode was investigated; the results are presented in Fig. 4. The tests carried out between 0 and 3 V at ambient temperature. The  $\text{Li}_2\text{MnSiO}_4/\text{Li}$  cell gives an initial discharge capacity of  $482 \text{ mAh g}^{-1}$ . During the second discharge, the capacity drastically reduces to  $181 \text{ mAh g}^{-1}$  under the same conditions described above. The irreversible capacity may be due to the formation a solid electrolyte interface during the cycling process [13–15]. In addition,  $\text{Li}_2\text{MnSiO}_4$  material presents a reasonable cycling profile, when using metallic lithium as a reference electrode.

Power performance and the dependence of specific capacitance on current density are shown in Table 1. It is clear that the specific capacitance decreases gradually with increasing current density. The reason for capacitance loss at high current densities could be explained by: (a) a large IR drop at high current densities leads to

**Table 1**  
Specific capacitance ( $C_s$ ) and specific energy ( $E$ ) and power ( $P$ ) densities of LMS/AC cell at various current densities.

Current density ( $\text{mA cm}^{-2}$ )	$C_s$ ( $\text{F g}^{-1}$ )	$E$ ( $\text{Wh kg}^{-1}$ )	$P$ ( $\text{W kg}^{-1}$ )
1	43.2	54	150
2	34.8	43	300
4	33.5	41	600
6	32	40	900
8	30.6	38	1200
10	29.6	37	1500



**Fig. 4.** Electrochemical performance of  $\text{Li}_2\text{MnSiO}_4/\text{Li}$  cell: (a) charge–discharge; (b) cycling profile.

small capacitance values; (b) activation and concentration polarizations at high current densities results in low utilization of the active materials. The data listed in Table 1 clearly reveal that the LMS/AC hybrid supercapacitor exhibits a high charge/discharge rate capability, a high specific energy, and stable cycle performance in a  $1.0 \text{ M LiPF}_6/\text{EC}:\text{DMC}$  electrolyte.

#### 4. Conclusion

A novel hybrid supercapacitor with  $\text{Li}_2\text{MnSiO}_4$  as the negative electrode and activated carbon as the positive electrode in  $1.0 \text{ M LiPF}_6/\text{EC}:\text{DMC}$  electrolyte has been developed. To our best knowledge, this is the first report of the assembly of an asymmetric supercapacitor with  $\text{Li}_2\text{MnSiO}_4$  as the electrode material. The initial specific capacitance obtained from the charge/discharge curve is  $43.2 \text{ F g}^{-1}$  at a  $1 \text{ mA cm}^{-2}$  current density. Specific capacitance decreases slightly with increasing current density and thereby shows that the LMS/AC cell has a high charge/discharge rate capability. The hybrid supercapacitor retains approximately 85% of its initial capacitance and exhibits a good cycleability with a high coulombic efficiency of greater than 99%, even after 1000 cycles.

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